THE ROLE OF ZETA POTENTIAL IN SAND FILTRATION

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TABLE OF CONTENTS

INTRODUCTION

The impurities which a filter may be called upon to remove in conventional water filtration vary both in character and in origin. Some suspended materials are introduced during pretreatment of the water and include such substances as hydrous aluminum or iron oxides, calcium carbonate crystals, and activated carbon. Natural waters, which are becoming increasingly diverse in their characteristics, can contribute particles such as clay, silt, and a wide variety of microorganisms to the filter influent. Filtration technology, which for a time remainded standardized, is now also becoming more diversified. Examples of this trend are the use of high rate and declining rate filtration, multi-media filters, larger grain sizes, and polymeric filtration aids. Development of a clear understanding of the filtration process would assist the design engineer to cope with increasing variation in raw water characteristics, and to obtain maximum benefits from new developments in filtration technology and equipment. The inability of current filtration theories to provide a useful basis for filter design is therefore a matter of some concern.

This report is written with two objectives: (1) to summarize the results of this research, and (2) to discuss and evaluate current filtration theory. The results of this research have been (1, 2) or will be (3) reported in more detail elsewhere.

EXPERIMENTAL STUDIES

Experimental investigations were conducted in three distinct phases: (1) batch studies of the aggregation of silica dispersions by iron(III), (2) continuous filtration experiments using iron(III) dispersions and packed columns which contained glass beads of relatively large diameter, and (3) continuous filtration experiments which used iron(III) floc and packed columns of Ottawa sand to simulate actual rapid sand filter operation. Chronologically,

phase 3 was conducted first, followed in order by phases 1 and 2.

Aggregation Experiments

The removal of particles of iron or aluminum hydroxide from suspension during rapid sand filtration involves chemical interactions between the suspended particles and the surface of the filter medium. The precise nature of these interactions and the parameters controlling their effectiveness are not well understood. Investigations of the aggregation of silica dispersions by iron(III) species have been made. In these systems the coagulation and restabilization of the silica dispersions are the result of interactions of iron(III) species with silica surfaces. These phenomena have been used as a qualitative measure of iron(III)-silica interactions. Pertinent data and results of these investigations will be presented here; a more extensive presentation and discussion of these studies will be available shortly (2).

Results

Representative results describing the coagulation behavior of iron(III)-silica systems as a function of the concentration of iron(III) added (C_t) are shown in Figures 1 and 2. Coagulation and restabilization were measured by light scattering and refiltration rate measurements. The critical coagulation concentration (c.c.c.) may be interpreted as the minimum C_t above which coagulation is produced. The critical stabilization concentration (c.s.c.) represents the C_t above which complete restabilization of the colloidal dispersion results. Coagulation occurs at applied iron(III) concentrations between the c.c.c. and the c.s.c. In the experiments reported here, the c.c.c. and c.s.c. are defined arbitrarily from a coagulation curve (scattering intensity or refiltration time vs. log C_t) by linearly extrapolating the portions of the curve in the coagulation region to ordinate values representative of samples containing no added iron(III).

The c.c.c. and c.s.c. values obtained from Figure 2 and from similar experiments are presented in logarithmic plots as a function of pH for two silica concentrations (using Min-U-Sil-5, a product of the Pennsylvania Glass Sand Corp.) in Figures 3A and B. Shaded areas indicate conditions under which iron(III) species coagulate these silica dispersions. In regions below the c.c.c. curves, insufficient iron(III) has been added to induce coagulation within the time of observation. Above the c.s.c. curves the silica suspensions are restabilized by sorption of positively charged hydroxo ferric species.

Included in Figure 3B is a log c.c.c. vs. pH curve obtained for the coagulation of negatively charged silver bromide sols by iron(III) (4). Hydrogen and hydroxyl ions are potential determining ions for silica, while the surface potential of a silver halide sol is unaffected by pH. Despite this restriction, the general shapes of the log c.c.c. -pH curves obtained for silica dispersions and silver bromide sols are remarkably similar. This observation suggests that solid surface-iron(III) interactions may be relatively independent of the chemical characteristics of the surface of the solid phase.

Figures 2 and 3 suggest that coagulation and restabilization are dependent upon the silica concentration or, more specifically, on the surface area of the dispersed phase. The influence of surface area is demonstrated by the data presented in Figure 4, where the c.c.c. and c.s.c. obtained using two forms of silica (Ludox, a product of E.I. Du Pont de Nemours and Co., and Min-U-Sil-5) are presented in logarithmic plots as a function of surface concentration (m^2/l) for three pH values.

Discussion

Various workers have shown that soluble hydroxo-metal complexes are readily sorbed at interfaces (5-7). This sorption will affect the equilibria resulting when iron(III) salts are added to aqueous suspensions. In undersaturated

solutions relatively little sorption is expected under conditions in which the aquo ferric ion predominates (pH < 2 in Figure 7), while the presence of such soluble hydroxo complexes as $FeOH^{2+}$, $Fe(OH)_2^{+}$, and $Fe_2(OH)_2^{4+}$ could be expected to lead to considerable sorption (2 < pH < 3 in Figure 7, Figures 5 and 6).

In oversaturated solutions, it seems plausible to consider that short chain multimeric hydroxo polymers which are kinetic intermediates in the precipitation of ferric hydroxide will tend to be sorbed at solid-liquid interfaces, possibly even more readily than their monomeric components. These species can therefore be removed from solution either by sorption on a solid surface or by continued reaction to form an insoluble precipitate.

Coagulation data obtained in the log C_t - pH region of undersaturation (Figure 3) can be compared with the hydrolysis and solubility equilibria depicted in Figure 7. At low pH values (pH < 1) the relative concentration of hydrolyzed iron(III) species is extremely small ($\left[Fe_x(OH)_y^{3x-y}\right] < 0.05\ C_t$); correspondingly, the c.c.c. is approximately that of a trivalent ion, and stoichiometric effects are not observed. The extent of hydrolysis increases with increasing C_t and pH; hydroxo ferric species that have a lower c.c.c. than Fe^{3+} are formed in significant concentrations, and surface area exerts an increasingly marked effect on coagulation.

Almost all coagulation experiments carried out at pH values above 3 represent conditions of oversaturation with respect to solid ferric hydroxide. Direct application of known hydrolysis equilibria is meaningful only under unsaturated conditions, or when metastable supersaturation can be demonstrated to exist. In a study of the solubility product of iron(III) hydroxide conducted in the pH range 1.7 to 2.7, Biedermann and Schindler (8) observed gradual changes in the composition of iron(III) solutions for up to 200 hours before a steady state was reached. These investigators demonstrated that metastable supersaturated solutions could be obtained, but only when C_t/Fe^{3+} was less than 2.5 and even very slight local excesses of base were avoided.

Coagulation of silica dispersions (and, by inference, iron(III)-silica interaction) also occurs at pH levels above the isoelectric point of ferric hydroxide, where iron(III) hydrolysis species bear a net negative charge. Under such circumstances, specific chemical forces appear to outweigh electrostatic repulsive forces, and permit the sorption of hydrolyzed iron(III) polymers which are negatively charged. These sorbed iron(III) species can cause particle aggregation either by sorbing directly on the surface of a second silica particle or by interacting with similar species previously sorbed on another particle. A three-dimensional network is formed between the particles. This interpretation is similar to the bridging models developed by Ruehrwein and Ward (9) and by La Mer and associates (10) for the flocculation of negatively charged particles by anionic polyelectrolytes.

At intermediate pH levels (approximately pH 4 to 7), aggregation of silica particles is accomplished by the interaction of positively charged iron(III) species with negative silica surfaces. Since stoichiometric effects are pronounced in coagulation under these circumstances, particle aggregation may not be attributed solely to double layer compaction by an indifferent electrolyte. In fact, it appears more reasonable to consider that the major interaction energy may continue to be chemical rather than coulombic. Particle aggregation occurs subsequent to iron(III) sorption, and at present it is not possible to distinguish between aggregation by a mechanism involving hydroxo ferric polymeric bridges, and by an interaction of silica particles whose negative charges have been neutralized by by sorption of positive hydroxo ferric species.

Restabilization is not observed in systems where the concentration of hydroxo ferric complexes is low, as in undersaturated iron(III) solutions at low pH ($pH < 2$). Silica dispersions do undergo restabilization in undersaturated solutions when sufficient soluble hydrolyzed iron(III) species are present. This corresponds approximately at the pH range 2 to 3. The observation that sols are restabilized by hydrolyzed iron(III) but not by aquo ferric ions is similar to that reported by Matijević et al for thorium(IV) (11).

Figure 6 combines the results of coagulation and restabilization experiments at pH 2.5 with sorption experiments made under similar conditions. Sorption curves are calculated from a modified form of the Langmuir equation, using the slope and intercept from the Langmuir plot (Figure 5), and using Min-U-Sil-5 concentrations of 20 g/l and 0.2 g/l (S = 168 m^2/l and 1.68 m^2/l, respectively). Restabilization is observed when the fraction of surface covered (θ) increases above about 0.9. Comparison of the observed data on coagulation and restabilization with the calculated curves for sorption indicates that at this low pH both coagulation and restabilization could be produced by sorption of soluble iron(III) species without significant surface area effects. Examination of Figure 3 indicates that these phenomena are in fact only slightly influenced by silica concentration in the pH range 2 to 3. It may be concluded that while stoichiometry in coagulation and restabilization is an indication that sorption is occurring, an absence of stoichiometry does not eliminate specific chemical sorption as a significant factor in these processes.

Restabilization is enhanced in solutions which are slightly oversaturated with respect to ferric hydroxide (pH 3 to 4). In such solutions, it is inferred that progressive hydroxylation and condensation can lead to multinuclear hydroxo species. At higher degrees of oversaturation, insoluble polymeric complexes of indefinite size, usually referred to as the insoluble metal hydroxide, are formed. Restabilization becomes retarded or obliterated in solutions that are highly oversaturated with respect to ferric hydroxide. With an increase in pH, the formation function ($[OH^-]$ bound per $[Fe(III)]$) increases and thus the net positive charge of the hydrolysis species decreases. In addition, the increased rate of ferric hydroxide precipitation may compete successfully with the sorption of incipiently formed soluble iron(III) species.

The results of these investigations suggest conclusions which appear to have significance in conventional water filtration, as follows:

(a) Polymeric hydroxo ferric species are specifically sorbed at interfaces. The occurrence and extent of this sorption may be determined by the characteristics of the iron(III) species. In many cases the surface characteristics of the solid phase may exert only slight influence on the sorption reaction. This observation suggests that the removal of iron(III) species in a filter bed may not be greatly affected by the type of filter material used in the bed. Important parameters include the concentration of iron(III) and the pH.

(b) Sorption of hydroxo ferric polymers on negatively charged silica continues at least to pH 10, indicating that charge effects alone cannot account for these interactions. Specific chemical interactions must be invoked in addition to electrostatic effects to explain the sorption of iron(III) at interfaces, at least in the pH range 2 to 10.

(c) The observed decrease of the c.c.c. with increasing pH above the neutral range (Figures 3 and 4) suggests that iron(III) removal during filtration will become less efficient with increasing pH at pH levels above the zero point of charge of the iron(III) system.

(d) The occurrence of restabilization suggests that sorption of iron(III) species is impaired by electrostatic effects after the silica surface has been "covered" by positively

charged hydroxo ferric species. Observations (c) and (d) suggest, therefore, that filtration of fresh iron(III) species will be optimum at pH levels in the neutral range.

(e) In addition to iron(III) concentration and pH, several other parameters can affect iron(III) sorption. These include the type and concentration of ligands which can compete with OH^- for coordination sites on the central metal ions, ionic strength, and the "age" of the iron(III) species. Effects of these parameters on the filtration process have been investigated, and the results are presented later in this report.

Filtration Experiments with Glass Beads

Colloid-chemical characteristics of both the suspended particles and the filter media can affect the attachment of hydrous ferric oxide particles at the solid-liquid interface within a filter bed. Silica will be assumed as the filter media throughout the subsequent discussion. Before considering the attachment of hydrous ferric oxide during filtration through packed silica columns, it is useful to examine the aqueous chemistry of iron(III).

The Aqueous Chemistry of Iron(III)

The addition of $Fe(ClO_4)_3$ to water in concentrations less than the solubility limit of ferric hydroxide leads to the production of soluble monomeric, dimeric, and perhaps trimeric hydroxo ferric complexes, in addition to the free aquo ferric ion. When a quantity of $Fe(ClO_4)_3$ sufficient to exceed the solubility limit is added, a series of hydrolytic reactions occurs, proceeding from hydroxo complex formation through colloidal hydroxo polymers and, finally, the

formation of a hydrous metal oxide precipitate (e.g. 12, 13).

Changes in the concentrations of various iron(III) species as a function of pH are presented in Figure 7. These curves are based on the addition of 10^{-3} moles/l of iron(III) to water. Appreciable quantities of soluble stable hydroxo ferric complexes are present only in the pH range 2 to 3. Minimum iron(III) solubility occurs at pH 8.0, the isoelectric point of the aqueous hydroxo ferric series. In many cases the isoelectric points of aqueous hydroxo metal complex series and the corresponding hydrous oxides are observed to be identical (14).

Iron(III) complex formation can occur with bases other than the hydroxide ion. Substances containing carboxyl or hydroxyl groups, silicates, inorganic phosphates, and, to a lesser extent, sulfates and chlorides, are able to coordinate with the free metal ions. The ability of these ions to compete with hydroxide ions is determined, to a large extent, by the ratio (ligand/OH^-). In many cases the presence of a competing ligand will lower the isoelectric point of the resulting precipitate. For example, when phosphate is coordinated with iron(III), fewer hydroxide ions are needed to produce an electrically neutral precipitate.

An important characteristic of hydroxo metal complexes is their tendency to be readily sorbed at interfaces (2, 5-7). Sorption of positively charged hydroxo ferric species produces coagulation and restabilization of negatively charged silver bromide sols (4, 15). The sorption of hydroxo ferric species on silica surfaces is described earlier in this report and elsewhere (2).

Aged iron and aluminum solutions exhibit different coagulation and filtration behavior than fresh solutions (2, 16, 17). Suspensions of several metal hydroxides show a marked decrease in pH with increasing time and temperature. It is significant for the purposes of this report to note that these colloidal species exhibit a pronounced decrease in chemical reactivity with time, as exemplified by inertness towards neutral salts and dilute acids. A model which provides an

explanation for these phenomena has been developed by Thomas (18) and extended by Pokras (19) and Stumm and Morgan (13). These investigators propose that metal hydroxides are comprised of polynuclear complexes in which hydroxide (ol) and oxygen (oxo) groups act as connecting links between the metal atoms. From the time that the salt of a polyvalent metal ion (e.g., $Fe(ClO_4)_3$) is added to water until the ultimate formation of the crystalline metallic oxide (e.g., Fe_2O_3), the central metal ions may be coordinated with aquo, hydroxo, or oxo groups. During this time the reactions aquo → simple hydroxo → ol → oxo are continually shifted to the right. Reactions involving simple hydroxo (those coordinated to a single metal atom) and aquo groups are rapid and reversible; reactions with ol groups are reversible and somewhat less rapid; oxo groups are almost inert. As a result, the precipitate becomes increasingly inert as time progresses.

Results

Investigations have been made of the removal of iron(III) species during passage through small packed columns containing glass beads. These experimental filtration runs, generally less than two hours in duration, provide qualitative evaluation of the influence of several chemical parameters on iron(III) removal. Attention was centered on the effects of pH, anion type and concentration, ionic strength, and ageing time. The experimental filters were 10 in. long, 1 in. in diameter, and were packed at a porosity of 40 per cent with spherical glass beads having a diameter of 4 mm. A filtration rate of 0.25 gpm/sq. ft. was employed; iron(III) concentration in the influent was 10^{-4} M. Some pertinent results will be summarized here; a more extensive description of these investigations will be available elsewhere (3).

Data obtained in the filtration of fresh and aged iron(III) solutions at three pH levels are presented in Figure 8. Ageing was accomplished by allowing the iron(III) solution to stir at room temperature (21 ± 1°C) at the desired pH

for a specified time period. Variation in ionic strength was minimized by addition of 3×10^{-3} M $NaClO_4$. The data in Figure 8 indicate that ageing has no effect on filtration at pH 5, retards filtration at pH 7, and improves filtration at pH 9.5.

Typical results of experiments conducted to investigate the effects of sulphate ions on the process are presented in Figure 9. Ionic strength was again controlled, in this case by varying the concentration of $NaClO_4$ added. The results indicate that the presence of sulphate ions improves filtration at pH 5, while exerting no effects of pH values of 7 and 9.5. The data presented in Figure 9 were obtained with fresh iron(III) solutions; similar results were obtained with iron(III) solutions which had been aged for 4 hours.

Ionic strength was varied from 3×10^{-3} to 3×10^{-1} by selective addition of $NaClO_4$. Variation in ionic strength over this range did not affect the removal of iron(III) at pH 7, while minor improvements were observed with increasing ionic strength at pH 9.5. At pH 5, filtration efficiency was unaffected by ionic strength below 3×10^{-2}, but improved significantly at an ionic strength of 3×10^{-1}. All experiments were made using fresh iron(III) dispersions.

Discussion

A consideration of the aqueous chemistry of iron(III) indicates that the chemical characteristics of iron(III) species are dependent upon such parameters as pH, ageing time, anion type and concentration, and ionic strength. The data obtained in this phase of the investigations indicate that the filtration of iron(III) dispersions is in fact influenced by these parameters and, by inference, by the chemical characteristics of the iron(III) species.

The results of these investigations form the basis for the following statements:

1. The optimum pH for the filtration of iron(III) dispersions varies with the extent to which ageing has occurred, the

presence of complex forming ligands other than OH^-, and the ionic strength of the solution. For fresh iron(III) dispersions in the absence of competing ligands and for ionic strengths less than approximately 3×10^{-2}, filtration is most efficient at a pH of about 7.

2. Ageing of 10^{-4} M iron(III) solutions at 21°C and ionic strength of ca 3×10^{-3} does not affect filtration at pH 5, impairs filtration at pH 7, and improves filtration at pH 9.5. It is useful to recall that the extent to which ageing does occur is also dependent upon temperature and iron(III) concentration, parameters which were not investigated in this research. From statements (1) and (2), it may be concluded that chemical ageing broadens the pH range over which filtration is effective, while reducing the efficiency of filtration at the optimum pH for the filtration of fresh iron(III) dispersions.

3. The pH range of efficient filtration is extended below pH 7 in the presence of 10^{-3} M sulphate ions; no effect is noted above pH 7 when the ionic strength is maintained constant. Sulphate concentrations of 10^{-4} M and less (ionic strength maintained ca 3×10^{-3}) have no effect at any pH investigated.

4. Increasing ionic strength improves the filtration of 10^{-4} M Fe(III) dispersions which do not filter well otherwise (e.g., fresh dispersions at pH 5 and 9.5). Sizable effects are noted only for high ionic strength at pH 5.

Filtration Investigations with Sand Columns

Investigations of the filtration of hydrous ferric oxide suspensions through sand beds have been made (1). Physical parameters such as sand size (U.S. standard sieve size 20-30), bed depth (24 in.), bed porosity (40 per cent), and filtration rate (2 gpm/sq. ft.) were held constant; characteristics of the aqueous suspending medium were varied.

Concentrated hydrous ferric oxide suspensions were prepared several hours prior to a filtration run from $FeCl_3$ and the necessary amount of NaOH to achieve the desired pH level. These suspensions were then applied to laboratory sand filters after dilution with waters containing 25 mg/l of chloride, sulphate, or phosphate ions, and also with demineralized water. Sodium was used as the common cation. Comparison was made of the effects of these ions on filtration at pH levels of 5, 7, and 9.5.

Results

Figures 10 to 13 depict the relationships observed between both head loss and bed penetration and the total quantity of iron(III) applied to the sand beds during the filtration runs. It is obvious that very significant differences in bed penetration and head loss occurred in these filtration runs. The only parameter which was varied in these experiments was the chemical composition of the aqueous suspending medium, and it is to this factor that these observed differences in filtration are ascribed.

Discussion

The results of this research provide experimental evidence that the surface properties of hydrous ferric oxide particles markedly affect their filtrability. These surface properties depend in turn upon the chemical composition of the aqueous phase. These chemical effects in the filtration

process are considered to result from interactions between the surface of the filter medium and the hydrolyzed iron(III) particles in suspension; this conclusion provides experimental support to sorption as a significant mechanism for particle removal in rapid sand filter.

Of the aqueous systems investigated, the type and concentration of anions produced the most significant effects on filter performance. The results indicate that in the pH range 5 to 7, filtration of these materials is affected much more significantly by the type of anion than by the pH of the system. The presence of phosphate ions was observed to be particularly influential in lowering the rate of head loss buildup and increasing bed penetration at all pH levels investigated. A range of phosphate concentrations from 10^{-4} to 10^{-3} M was employed. Sulphate ions were observed to impair filtration at pH 5, exert minor effects at pH 7, and improve filter performance at pH 9.5.

The effects of sulphate ions on the filtration of hydrous ferric oxide precipitate which have been preformed in concentrated iron(III) solutions are therefore different from the effects described earlier for the filtration of iron(III) dispersions in which the iron(III) precipitates are formed in more dilute systems. These earlier investigations are more representative of conditions in conventional water treatment plants. This observation suggests that filtration investigations using preformed hydrous metal oxide precipitates, even when subject to close laboratory control, may be unable to represent conditions of practical interest.

FILTRATION THEORIES

To assist in the presentation of a logical and coherent discussion of filtration theories, it is useful to classify them. A theory of water filtration might be described as conceptual or empirical, mathematical or descriptive, and based on laboratory or field experimentation. For the purposes of this report,

filtration theories will be described as physical or chemical. Theories which consider physical characteristics of the filter bed, its method of operation, and the suspension being treated will be classified as physical filtration theories. The great majority of these theories deal with media size, filtration rate, and water temperature. Theories which consider the chemical characteristics of the aqueous phase and the surface characteristics of the suspended particles and the filter media will be classified as chemical filtration theories.

Physical Filtration Theories

The investigation of K. J. Ives (e.g., 20-23) are outstanding in the field of water filtration theory, and will be summarized here. Ives begins with two equations suggested by Iwasaki in 1937 (24):

$$-\frac{\partial C}{\partial L} = \lambda C \tag{1}$$

and

$$\frac{\partial \sigma}{\partial t} + \frac{v}{(1-f_\sigma)} \frac{\partial C}{\partial L} = 0 \tag{2}$$

where C = volumetric concentration of material entering a unit volume of filter, L = filter depth, λ = coefficient of proportionality, also termed the filter coefficient, t = filtration time, σ = volume of suspended material retained per unit of filter volume, f_σ = the porosity of the deposited material, and v = superficial filtration velocity.

Equation 1 states that the removal of suspended particles is proportional to the concentration of particles present in the water. This assumption has been made by most other researchers in the field of water filtration (e.g., 25-28). A rational basis for this assumption has been provided by investigators in aerosol filtration (29-30), together with supporting experimental evidence (31). Equation 2 is based on a mass balance and states that the volume of

material accumulated in the filter equals the volume removed from suspension. This assumes that (a) the density and porosity of the deposited material do not change during the course of a filtration run, and (b) biological and chemical reactions do not cause soluble materials either to accumulate in the deposits or to be released from them.

The filter coefficient is altered by the accumulation of deposited material in the filter. Ives proposes that

$$\lambda = \lambda_o + c\sigma - \frac{\phi \sigma^2}{(f-\sigma)} \tag{3}$$

where λ_o, c, and ϕ are filter coefficient constants, and f = the initial filter bed porosity. Equation 3 is an empirical expression which describes the variation of the filter coefficient with the specific deposit.

Substitution of Equation 3 in Equation 1 yields

$$-\frac{\partial C}{\partial L} = \left(\lambda_o + c\sigma - \frac{\phi \sigma^2}{(f-\sigma)}\right) C \tag{4}$$

Equation 2 and 4 describe the changes in concentration and specific deposit in time and space. They are not amenable to explicit solution, but have been solved numerically by Ives with the aid of a digital computer.

Based on experimental evidence, Ives proposes that

$$\frac{\partial h}{\partial L} = \left(\frac{dh}{dL}\right)_o + k\sigma \tag{5}$$

where h is the head loss, $(^{dh}/_{dL})_o$ is the head loss per unit of depth at t = 0 ($\sigma = 0$), and k is a head loss constant. Equation 5 describes the dependence of the hydraulic gradient on the specific deposit. When combined with Equation 2 and 4 it provides for numerical calculation of the changes in head loss in time and space.

Ives has demonstrated that Equation 2, 4, and 5 were able to reproduce successfully experimental curves obtained in the laboratory for both the change of concentration of suspended materials and the increase of head loss during a

filtration run. The equations provide for prediction of the effects on filter performance of changes in bed depth, and the concentration of suspended materials applied to the filter.

It is important to note that Equations 2, 4, and 5 contain five constants, λ_o, c, ϕ, k, and f_σ. Four of these (λ_o, c, ϕ, and k) are affected by characteristics of the filter bed, its mode of operation, and the suspension being filtered. The last (f_σ) may be only a characteristic of the materials in suspension. In order to use the equations developed by Ives, it is necessary for the filter designer to determine experimentally a set of five coefficients for each filter bed, flow rate, and pretreatment condition he may wish to consider.

An evaluation of the effects of pertinent filtration variables on these five experimental coefficients would simplify the application of Ives' equations to filter design and could also provide them with a rational basis. Ives and Sholji (32) have investigated the effects of certain physical filtration variables (viz., sand, flow rate, and water temperature) on the filter coefficient constants λ_o, c, and ϕ. Their stimulating paper presents a valuable comparison of current filtration theories, which need not be repeated here; it does not suggest a more direct method for obtaining these coefficients, nor does it offer convincing mechanistic insights into the filtration process.

Mathematical formulations describing the effects of physical variables on the filtration process have been proposed by many investigators. Based on field observations reported by the ASCE (33), G. M. Fair (34), proposes the following empirical equation:

$$L_A = K_A d_s^{5/3} \left(\frac{60}{T_F + 60} \right) \qquad (6)$$

where L_A = depth of penetration (inches) for a terminal bed loss of 8 feet, a filtrate with a turbidity $\leq$ 2 mg/l, and a filtration rate of 2 gpm/sq.ft.,

d_s = sand size (mm), T_F = water temperature ($^{\circ}F$), and K_A = coefficient which varies with the raw water quality. Stanley (35) formulates the following equation for the filtration of iron(III) flocs in laboratory experiments:

$$L_s = K_s d_s^{2.46} Q^{1.56} \qquad (7)$$

where L_s = depth of penetration (inches) for a terminal head loss of 8 feet and a water temperature of 25°C, Q = filtration rate (gpm/sq.ft.), and K_s = 6.4. Equations similar to these have been developed by other investigators (e.g., the empirical equations reported by Ling (36), and the conceptual relationships proposed by Hall (26)). Valuable descriptive statements concerning the effects of these and other physical variables on the performance of filters have been made by a number of investigators (e.g., 25, 37-48).

When contrasted with the models developed by Ives and others (e.g., 27-28), these relationships appear quite straightforward. Despite their relative simplicity, however, equations of this type have not found wide application in engineering practice. Indeed, the development of the computer is eliminating the need for mathematical simplicity in engineering formulations.

Whether simple or complex, it can be stated that current filtration theories provide an interpretation of observed facts concerning the particular filters and suspensions studied by each investigator. It must also be stated, however, that no one of these theories can predict the performance of a filter treating a given suspension without extensive laboratory testing. No one of these theories is capable of predicting accurately the performance of the same or another filter treating another suspension.

Ives and Sholji (32) compare several filtration theories by evaluating the relationships which these theories predict between the filter coefficient (λ) and the variables sand size (d_s), filtration velocity (V) and water viscosity (μ). The results are remarkable in their disagreement. Representative results are as follows:

Ives and Sholji (32)	$\lambda \propto \frac{1}{d_s V}$	(8a)
Hall (26) straining	$\lambda \propto \frac{1}{d_s^{2.5}}$	(8b)
settling	$\lambda \propto \frac{1}{d_s V \mu}$	(8c)
Mackrle and Mackrle (28)	$\lambda \propto \frac{\mu^{\frac{1}{2}}}{d_s^2 V}$	(8d)
Stanley (35)	$\lambda \propto \frac{1}{d_s^{2.46} V^{1.56}}$	(8e)
Mintz and Krishtul (27)	$\lambda \propto \frac{1}{d_s^{1.7} V^{0.7}}$	(8f)
Stein (25)	$\lambda \propto \frac{1}{d_s^3}$	(8g)

The filter coefficient is thus reported to vary with $d_s^{-1.0}$ to $d_s^{-3.0}$, with $V^{-0.7}$ to $V^{-1.56}$, and with $\mu^{-1.0}$ to $\mu^{+0.5}$.

It does not appear unfair to state that current physical theories of filtration are either too simple to be flexible enough to apply in practice, or too complex (i.e., require an excessive amount of experimentation) to be useful. In either case, they disagree to such an extent that their general applicability may be questioned.

Chemical Filtration Theories

In recent years some investigators have directed attention to the effects of chemical parameters on the filtration process. To some extent these investigations have been motivated by the inability of physical theories to explain observed filtration data or to predict filter performance. It is profitable to summarize the development of these theories to date (1966). With a few exceptions, these theories have not advanced to the state where they can be expressed in mathematical language, and are presented in a descriptive form.

Stanley (35) reports that hydrous ferric oxide particles are filtered most readily in the pH region surrounding their isoelectric point. The presence of

500 mg/l of NaCl, Na_2SO_4, or $MgSO_4$ was observed to increase the rate of penetration significantly. Stanley proposes that the suspended particles are removed most easily when their electrostatic repelling forces are at a minimum. Cleasby and Baumann (49) conclude that electrostatic forces are primarily responsible for the removal of hydrous ferric oxide particles. Hunter and Alexander (50) reversed the surface charge on silica sand columns from negative to positive by adsorption of hexadecyltrimethyl ammonium ions and substantially increased the ability of these columns to remove negatively charged kaolinite particles from suspension. Davis and Borchardt (51) report that coagulating chemicals are necessary in the influent to a filter if it is to remove algae and particles of activated carbon effectively, conclude that chemical factors are important, and suggest that electrostatic effects may be significant. In contrast, Jordan (52) operated gravel filters for 65 days in order to develop a Schmutzdecke and then observed that the filtration of clay suspensions improved as the zeta potential of the applied clay particles was made increasingly negative. Mackrle and Mackrle (28) consider that the attachment of a suspended particle to the surface of the filter media is controlled by van der Waals forces and assume that electrostatic forces are insignificant. Conley and Pitman (53) observed that the application of a polyacrylamide to the filter influent improved the filtrability of alum floc particles and postulated that the polymers bound the floc particles to the filter and to each other. This polymer is nonionic, indicating that chemical effects other than those of coulombic origin can be significant.

Sorption of suspended particles on the surface of the filter media has been proposed by Stein (25), Ives (22), Camp (43), Fox and Cleasby (45), O'Melia and Crapps (1), and several other invesitgators as an important factor in filter performance. Relatively few investigations have been made, however,

in which attention was focused on the chemical aspects of the process. The investigations summarized earlier in this report and elsewhere (1, 2, 3) centered on the colloid chemical aspects of the process, as did the research of Ives and Gregory (54). The results of this latter investigation will be summarized here.

Ives and Gregory (54) modified the mathematical model for diffuse layer interactions developed by Verwey and Overbeek (55) to account for the interaction of particles with unequal surface potentials. These authors then applied this model to their own observations of the filtration of polyvinyl chloride spheres (diam. ca. 1.3 microns) through sand beds, and to the data reported by O'Melia and Crapps (1) for the filtration of hydrous ferric oxide particles (diam. ca. 20 microns). Calculations of zeta potentials were made for the sand beds from streaming potential measurements, and for the suspended particles from electrophoretic mobility determinations. Combined interaction energies were calculated by combining the electrostatic effects of the diffuse layer interactions with the attractive energy resulting from van der Waals forces. Calculation of van der Waals forces required an estimate of the Hamaker constant in aqueous systems.

These authors conclude that diffuse layer interactions may not be invoked to explain the transport of particles from the bulk flow to the vicinity of the grain surfaces. Increasing potential energy barriers were found to correlate with decreased filtration efficiency. Despite the mathematical elegance of the theory, a mathematical relationship between chemical parameters and filter performance was not obtained. Ives and Gregory note that some particles always are retained, and propose that removal mechanisms which are independent of surface forces (e.g., interstitial straining) may be operative. It seems plausible to suggest that (a) experimental evaluations of zeta potentials are subject to considerable uncertainty,

(b) the model is sensitive to the estimated value of the Hamaker constant, which cannot be determined with precision, and, most significantly, (c) the mathematical model reflects only one of many types of colloid-chemical reactions which can occur at the water-filter interface.

In the same manner as their physical counterparts, chemical filtration theories (a) show considerable disagreement among themselves, and (b) are unable to provide a means for predicting filter performance. Water filtration practice remains an art.

OUTLINE OF A FILTRATION MODEL

It is instructive and, in the opinion of this writer, essential, to consider suspended particle removal within a filter bed in at least two separate and distinct steps: (1) a transport step, and (2) an attachment step. Particle transport is a physical-hydraulic process and is principally affected by those parameters which govern mass transfer. Particle attachment is basically a chemical process, and is influenced by both physical and chemical parameters.

Most investigators of water filtration have considered only the effects of physical parameters (principally sand size and flow rate) on the filtration process. The results, as mentioned previously, are remarkable in their disagreement. It is proposed that this lack of agreement may have originated from two causes (1) the possibility of more than one transport mechanism simultaneously being effective has not been adequately investigated, and (2) significant chemical variables are not known and consequently have not been controlled. It seems plausible that concepts of mass transfer employed by investigators of aerosol filtration may provide an insight into transport mechanisms in water filtration, and a brief discussion of some work in this area appears useful. An attempt will also be made to formulate chemical models which can describe the attachment step in water filtration.

The Transport Step

Friedlander (30) has successfully correlated data on aerosol filtration by fibrous filters operated at low flow rates with the following equation:

$$\eta = 6 N_{pe}^{-2/3} N_{re}^{1/6} + 3 N_r^2 N_{re}^{1/2} \qquad (9)$$

where N_{pe} = Peclet number, N_{re} = Reynolds number, N_r = direct interception parameter (the ratio of the particle diameter, d_p, to the cylindrical collector diameter, d_c), and η = single fiber removal efficiency. The Peclet number is a measure of the ratio of transport by convective forces to transport by molecular diffusion and is equal to Vd_c/D_{bm}, in which V = fluid (and particle) velocity at an infinite distance from the collector and D_{bm} = particle diffusivity. The Reynolds number is equal to $\rho V d_c/\mu$, where μ = fluid viscosity and ρ = fluid density. In a fibrous filter bed the removal efficiency of a single fiber (η) is described as follows (30):

$$\eta = \frac{\pi d_c}{4(1-f)} \ln \frac{C_1}{C_2} \qquad (10)$$

where C_1 and C_2 are the inlet and outlet concentrations for an aerosol passed through the filter.

While Equation 9 is derived empirically, Friedlander provides a convincing rational basis for the form of the equation. Among the assumptions made are the following:

(1) Diffusion is assumed as the transport mechanism. Direct interception is introduced as a boundary condition on the diffusion equation. Such transport mechanisms as sedimentation and inertial impaction are not considered.

(2) $N_{pe} \gg 1$. This assumes that transport by convective forces is large compared to molecular diffusion in the bulk flow. Molecular diffusion is assumed to predominate in a thin boundary layer near the fiber surface and controls the over-all transfer rate.

(3) $N_{re} < 1$. Lamb's solution for the velocity distribution in viscous flow around a cylinder (56) is assumed.

The quantity $6\ N_{pe}^{-2/3}\ N_{re}^{1/6}$ in Equation 9 represents the contact efficiency for small particles ($N_r \rightarrow 0$) where pure diffusion controls, while the quantity $3\ N_r^2\ N_{re}^{1/2}$ represents the contact efficiency where direct interception controls.

Equation 9 predicts a minimum in the relationship between contact efficiency and particle size. Particle diffusivity may be expressed as:

$$D_{bm} = \frac{kT}{3\pi\mu d_p} \qquad (11)$$

where k = Boltzmann's constant and T = absolute temperature. Substituting Equation 11 in Equation 9 one obtains

$$\eta = \frac{3.42\ k^{2/3}\ T^{2/3}\ \rho^{1/6}}{\mu^{5/6}\ d_p^{2/3}\ d_c^{1/2}\ V^{1/2}} + \frac{3\ d_p^2\ \rho^{1/2}\ V^{1/2}}{d_c^{3/2}\ \mu^{1/2}} \qquad (12)$$

By differentiating Equation 12 with respect to d_p and equating to zero, the following expression is obtained:

$$d_{pm} = 0.489\ \frac{(k\ T)^{1/4}}{(\rho\ \mu)^{1/8}}\ \left(\frac{d_c}{V}\right)^{3/8} \qquad (13)$$

where d_{pm} = diameter of particle having the minimum contact efficiency.

It is recognized that Equation 9, 12, and 13 cannot apply directly to water filtration. Sand grains do not resemble cylindrical fibers in shape. The porosity of a sand filter is normally about 0.4, while the fiber mats used in aerosol filtration typically have porosities greater than 0.9. Despite these and perhaps other limitations, an attempt will be made to show that filtration models such as Friedlander's can provide a considerable insight into the transport mechanisms in water filtration.

Calculated "single grain" contact efficiencies for a typical rapid sand filter are presented as a function of the diameter of the particles in suspension in Table 1.

The over-all contact efficiency of the filter bed is also tabulated. The results of these calculations are not in disagreement with water filtration practice.

Most previous investigators of rapid sand filtration (e.g., 22, 35) including this writer (1) have concluded that diffusion is insignificant as a transport mechanism in the process. Calculation of d_{pm} in Equation 13 for the filtration conditions assumed in Table 1 indicates that the diameter of the particle having a minimum contact efficiency is approximately 3μ. The calculations presented in Table 1 indicate that contact efficiency increases with decreasing particle size below 3μ. Data reported by Robeck (57) from the Gaffney, South Carolina filtration plant indicate that the great majority of particles in the filter influent were smaller than 3μ in diameter. These observations suggest that diffusion be reevaluated as a transport mechanism in conventional water filtration.

The relationship between the impediment modulus and the single fiber collection efficiency can be determined by combination of Equations 1 and 10.

$$\lambda = \frac{4\,(1-f)}{\pi\, d_c}\,\eta \qquad (14)$$

Substituting Equation 14 in Equation 9 one obtains:

$$\lambda = \frac{4.35\,(1-f)\,k^{2/3}\,T^{2/3}\,\rho^{1/6}}{d_p^{2/3}\,\mu^{5/6}\,d_c^{3/2}\,v^{1/2}} + \frac{3.82\,(1-f)\,d_p^{2}\,\rho^{1/2}\,v^{1/2}}{\mu^{1/2}\,d_c^{5/2}} \qquad (15)$$

Precise calculations of λ using Equation 15 are not warranted. It is instructive, however, to consider the form of the equation. For the case where and are constant, Equation 15 may be rewritten as follows:

$$\lambda = \frac{K_1\,T^{2/3}}{d_p^{2/3}\,\mu^{5/6}\,d_c^{3/2}\,v^{1/2}} + \frac{K_2\,d_p^{2}\,v^{1/2}}{\mu^{1/2}\,d_c^{5/2}} \qquad (16)$$

Table I

CONTACT EFFICIENCY OF A TYPICAL* RAPID SAND FILTER

	Diameter of Suspended Particles (microns)					
	0.1	0.3	1.0	3.0	10	30
$6\ N_{pe}^{-2/3}\ N_{re}^{1/6} \times 10^6$ (Diffusion)	1880	905	406	195	87	42
$3\ N_r^2\ N_{re}^{1/2} \times 10^6$ (Direct Interception)	0.098	0.88	9.8	88	987	8800
$\eta \times 10^6$ #	1880	906	416	283	1065	8842
Contact Efficiency+ (per cent)	82.7	57.0	32.3	23.0	63.0	99.9

* A rapid sand filter with d_c = 0.5mm, V = 2 gal/min/sq.ft., f = 0.40, μ = 1 cp, and L = 24 in. has been assumed.

\# Calculated from Equation 9.

\+ Calculated from Equation 10.

Equation 16 predicts that for pure diffusion, λ will be proportional to $d_c^{-3/2}$ and $V^{-1/2}$, while for direct interception λ will vary with $d_c^{-5/2}$ and $V^{+1/2}$. In other words, for the case of the filtration of a dispersion with a heterogeneous size distribution and where contacts are produced by pure diffusion coupled with direct interception, no unique proportionality may be expected to exist between contact efficiency and the two water filtration variables most commonly investigated, sand size and filtration rate. Additional transport mechanisms may also influence the process, and will then further complicate the effects of d_c and V on contact efficiency. This observation provides one possible explanation for the disagreement noted in Equation 8a to 8g.

Equation 16 indicates that contact efficiency is proportional to $d_p^{-2/3}$ for pure diffusion and d_p^2 for direct interception, and is therefore much more sensitive to changes in d_p than in d_c, V, or μ. Investigations into the area of transport mechanisms in water filtration might profitably direct some attention in this direction. Furthermore, some insight into the effects of d_p on filter efficiency could affect pretreatment practice.

The Attachment Step

The attachment of a suspended particle to the solid-liquid interface presented by the filter (i.e., either to a sand grain or to another particle which has previously been retained in the bed)can be controlled by the surface properties of the respective materials. Particle attachment, like particle transport, can be accomplished by a number of different mechanisms. Two models which appear to have both theoretical interest and practical significance will be summarized here: (a) the interacting double layer model(55),and (b) the chemical bridging model developed by Ruehrwein and Ward (9) and La Mer and associates (10).

Double Layer Interactions

The simplest colloid-chemical model that can be used to describe the interactions between suspended particles and the surface of the filter is based on the theory of electrical double layer interactions. Application of this theory assumes that the net interaction between a suspended particle and the filter surface can be described by a quantitative combination of van der Waals attraction with the coulombic repulsion or attraction of the two double layers.

An electric double layer exists at every interface between a solid and an aqueous phase. The solid side of the interface assumes an electrostatic charge (the primary charge) which may be either positive or negative. The origin of the primary charge depends on the chemistry of the substance. An equivalent number of counter-ions of opposite charge form a diffuse layer in the aqueous phase.

When a suspended particle approaches the surface of the filter, the two diffuse ion atmospheres begin to interact. If both double layers are of similar sign, this interaction will result in the formation of a repulsive potential energy, V_R, that varies approximately in an inverse exponential manner with the separating distance, x. The van der Waals attractive forces also increase as the particles approach each other. For large particles the attractive potential energy, V_A, varies inversely with x^2. Summation of V_R and V_A yields a curve describing the variation

in net interaction energy ($V_R - V_A$) as a function of **x**. For sufficiently strong repulsive interactions between the particles, a net repulsion can predominate over intermediate separating distances, thereby impairing particle attachment.

The van der Waals attractive potential is virtually independent of the composition of the aqueous phase. The coulombic potential energy, however, may be controlled by characteristics of both the solid and the aqueous phases. With some substances the double layer is created by chemical interaction with potential determining ions, and the surface electrical potential is determined by the concentration of these ions in solution. In other systems (e.g., the clay minerals), the double layer may originate from imperfections in the crystal lattice, with the result that the surface charge density is fixed and constant.

In applying this model to particle attachment in sand filtration the following observations may be made:

(1) Hydrogen and hydroxide ions can be potential determining ions for several metallic oxides, including SiO_2, Fe_2O_3, and Al_2O_3. At a given pH these materials will therefore have a constant surface potential. Changes in pH will alter the surface electric potential, modify the variation of V_R with **x**, and affect particle attachment. Silica is negatively charged above the pH range 1.5 to 2, while the isoelectric points of Fe_2O_3 and Al_2O_3 are in the neutral and alkaline pH regions (14). For Fe(III) and AL(III), the isoelectric points of "amorphous" hydroxides, "hydrous" oxides, and crystalline oxides can differ (14). At pH levels above the isoelectric point of the suspended particles, an electrostatic repulsion exists between the sand and the particles as a result of the interaction of the two negatively charged double layers. Van der Waals attractive forces will predominate in the isoelectric region of the particles and will be augmented by

coulombic attraction at lower pH levels. This model predicts that particle adhesion to the sand grains will be promoted at low pH levels; suspended particle cohesion to previously filtered particles will be optimum at their isoelectric point.

(2) For constant potential surfaces the addition of a neutral salt (indifferent electrolyte) will not change the surface potential, but will alter the V_R vs. x curve. Increase in the ionic strength of the solution compresses the diffuse layer and produces a decrease or elimination of any net repulsive energy barrier between similarly charged substances. For surfaces with a constant charge density, the addition of an indifferent electrolyte will lower the surface potential and compress the double layer, both effects tending to enhance attachment of similarly charged surfaces. The double layer model thus predicts that filtration at pH levels above the isoelectric point of the particles in suspension will improve with increasing ionic strength.

(3) The number of atoms per unit volume in each of the interacting materials affects the magnitude of the Hamaker proportionality constant, A, used in the determination of the van der Waals attractive potential energy. Mackrle and Mackrle (28) have noted that in water filtration, variation in A is produced primarily by variation in the density of the suspended particles. Increase in particle density produces an increase in A, an increase in V_A, a reduction or elimination of the potential energy barrier, and, consequently, improved filtration.

The Chemical Bridging Model

Natural and synthetic macromolecules have a pronounced effect on the stability of colloidal dispersions, and polyelectrolytes have been used successfully as "filter conditioners" (53) and as aggregating agents in water purification and sludge conditioning. It is essential to recognize that particle attachment brought about by these materials cannot be characterized by the double layer model. La Mer and co-workers (10) and others (9,59) have developed a chemical bridging theory which provides a more acceptable model for understanding the ability of polyelectrolytes to induce particle attachment in colloidal systems.

In its simplest form the chemical bridging model proposes that a polymer molecule can attach itself to the surface of a colloidal particle at one or more adsorption sites, with the remainder of the molecule extending into the solution. These extended segments can then interact with vacant adsorption sites on another surface, forming a chemical bridge between the two surfaces. Failing to find a suitable adsorption site on another surface, the extended segments can eventually adsorb at other sites on the original particle.

Adsorption of the polymer segments on a particle surface may occur by a number of different physical and chemical interactions, depending upon the characteristics of both the polymer and the surface. When polymer and surface are of opposite charge, coulombic attraction is often invoked as the basis for the interaction. It is important to recognize, however, that specific chemical forces can outweigh electrostatic forces in many cases. Adsorption of anionic polymers or negative surfaces is common (10, 60-62). Postulated interactions include ion exchange, hydrogen bonding, and the formation of coordinative bonds and linkages.

Some significant ramifications of this model when applied to water filtration are:

(1) In many cases optimum bridging is achieved with polymers having the same sign as the surface electric charge of the particles.

(2) Optimum attachment occurs when only a fraction of the available sites on each surface are covered. La Mer notes optimum aggregation of negatively charged particles with anionic polymers when one-half of the available sites are covered. Complete coverage of the suspended particles and the filter surface would therefore prevent particle attachment during filtration. This suggests that (a) optimum polymer dose should be proportional to the concentration of the suspended particles or, more precisely, the concentration of surface applied to the filter, and (b) it is possible to render a polymer ineffective by overdosing.

(3) The possibility of extended segments folding back on the surface of the suspended particles suggests that the time from the application of the polymer to filtration can influence the effectiveness of the polymer in bringing about particle attachment.

(4) Polymers will have a pronounced effect on the density, shear strength, and compressibility of the material deposited in the filter bed.

SUMMARY

In order to describe particle removal within a filter bed, it is necessary to consider filtration as a combination of particle transport and particle attachment. Surprisingly, such a distinction is not often found in the literature dealing with water filtration. In a conventional coagulation process it would be useless to design and construct the flocculation tank without first providing for the destabilization of the colloids which are to be removed. In like manner, contact between a suspended particle and the filter medium is ineffectual if the particle does

not adhere to the surface of the filter. Certainly particle destabilization in the conventional coagulation process is of little use if facilities are not provided to bring these destabilized particles into contact and allow them to grow to a suitable size. Similarly, in water filtration, particle "stickiness" is fruitless if the particles do not contact the solid-liquid interface provided by the filter.

Particle transport can be influenced by sand size, filtration rate, fluid temperature, and the size and density of the suspended particles. No research, systematic or otherwise, has experimentally investigated the effects of these latter two parameters (ρ_p and d_p) on the filtration process. Based upon what is admittedly a lengthy extrapolation of aerosol filtration theory, it seems plausible to propose that particle transport in water filtration may be influenced more by suspended particle size than by any other parameter.

Particle attachment is brought about by colloid chemical forces. Electrostatic interactions can be significant, but have not been observed to control particle attachment. The double layer model is unable to provide either a conceptual or an operational prototype for filter performance. Electrophoretic mobility (zeta potential) measurements, which afford a very rough measure of electrostatic interaction, cannot provide an accurate estimate of the forces affecting particle attachment in water filtration. The usefulness of zeta potential as a parameter for predicting filter performance is therefore quite limited.

This research has demonstrated that the effects of chemical parameters on filter performance are very significant, interrelated, and quite complicated. In attempting to provide a model for the attachment step in water filtration it is again useful to consider the destabilization step of the coagulation process. It is important to recognize that here again the double layer model has not provided a useful prototype for natural systems of interest. A chemical bridging

model has been developed which is of considerable assistance in understanding the effectiveness of polymeric coagulants. The destabilization of colloids by hydrolyzed iron(III) and aluminum(III) appears to have some characteristics of both the double layer and bridging models, and requires an understanding of the aqueous chemistry of these metal ions. The results of this research indicate that these same statements apply to the filtration of iron(III) dispersions.

Based on a consideration of the aqueous chemistry of iron(III), chemical parameters which could influence particle attachment in water filtration include ageing time, temperature, iron(III) concentration, type and concentration of anions, and pH. In separately evaluating the effects of these parameters, a considerable amount of overlapping is observed. For example, no unique relationship exists between pH and filtration efficiency. The filtration of fresh iron(III) dispersions is optimum at pH ca. 7; ageing reduces efficiency at pH 7 and improves removal at pH 9.5.

Possible causes for the lack of agreement among filtration theories might include the following:

1. There can be no doubt that water filtration is affected by both physical and chemical parameters. Investigations of the effects of physical parameters (e.g., filtration rate) can only be compared if the effects of chemical parameters are constant. Similarly, analyses of the effects of chemical parameters (e.g., pH) can be facilitated if physical parameters are constant. For most investigations this is not the case.
2. There are no grounds for assuming a priori that only one transport mechanism is significant in water filtration. Ives has noted that gravitational setting (20) and diffusion

(63) can be significant. Friedlander (30) has successfully correlated data for aerosol filtration by assuming that diffusion and direct interception are important at low air flow rates.

3. Similarly, there are no grounds for assuming a priori that diffuse layer interactions are the only colloid chemical forces controlling particle attachment.

Camp (43) has stated, "It is the writer's opinion that pilot plant studies of filtration must be widely used if worthwhile improvements are to be made in filtration." Mintz (64) has presented the following statement:

> "There are complicated interrelations among many factors affecting the performance of rapid filters. These interrelationships vary with seasonal changes in the quality of raw water, chemical treatment, output, and load changes. Therefore, it is apparent that an attempt to work out an exact mathematical description, with theoretical constants, of the filtration process to hold for any conditions of filter operation is bound to fail. Obviously, it will be always necessary to determine the parameters of the process experimentally. The task of the theory is to provide a rational experimental procedure and a rational method of working out the experimental data so as to get the results required for engineering practice".

The rational experimental procedure requested by Mintz (64) is a prerequisite to the pilot plant studies suggested by Camp (43). It is also evident that the development of a rational experimental procedure requires some knowledge of the parameters which can affect the process. Parameters such as suspended particle size, pH, age of the hydrous oxide floc particles, and, to a lesser extent, the ionic composition of the water, can be controlled by pretreatment practice. The results of this research indicate that all can affect filter performance.

LEGENDS

Figure 1. Representative curves for coagulation of Ludox and Min-U-Sil-5 suspensions. Turbidity changes as a function of the concentration of iron(III) applied at pH = 5. From these and similar data the c.c.c. and c.s.c. are observed to vary with the silica concentration, or more specifically, the surface concentration of the solid phase.

Figure 2. Representative curves for coagulation of Min-U-Sil-5 suspensions (20 g/l). Refiltration time changes as a function of the concentration of iron(III) applied. From these and similar data the c.c.c. and c.s.c. are observed to vary with pH.

Figure 3. Log C_t - pH domains of coagulation and restabilization obtained at two Min-U-Sil-5 concentrations. The c.c.c. (O) and c.s.c. (Δ) data are obtained from curves similar to those presented in Figures 2 and 3.

Figure 4. Log C_t - S domains of coagulation and restabilization obtained at various pH values. The c.c.c. and c.s.c. data are obtained from curves similar to those presented in Figures 2 and 3: (O), c.c.c., Min-U-Sil-5, by light scattering; ($\bullet$), c.s.c., Min-U-Sil-5, by light scattering; (∇), c.c.c., Min-U-Sil-5, by refiltration rate; ($\square$), c.c.c., Ludox, by light scattering. Solid lines describe the boundaries between coagulated and uncoagulated or restabilized dispersions. The c.c.c. and c.s.c. are observed to vary with the surface concentration of the solid phase. Light scattering and refiltration rate measurements appear to be complementary techniques for evaluating coagulation. The dashed line is the calculated variation of log $C_{t\theta}$ with log S, assuming $\Gamma_m = 2.3 \times 10^{-6}$ moles/m^2, $K = 10^{-7}$ l/mole, and $\theta = 0.4$ in the Langmuir adsorption equation (see Figure 5), $C_{t\theta}$ = the concentration of applied iron(III) necessary to produce a certain fraction of surface coverage (θ).

Figure 5. Linearized Langmuir plot for the sorption of iron(III) on Min-U-Sil-5;

$$\frac{C_a}{S} = \Gamma = \frac{\Gamma_m K C_e}{1 + K C_e} \qquad (17)$$

where C_e and C_a = the concentrations of residual and sorbed iron(III) (moles/l), respectively; Γ_m = sorption capacity (moles iron(III)/m^2); S = surface area of silica in the dispersion (m^2/l), and K is a constant (in the Langmuir model K is the equilibrium constant for the absorption-desorption reaction).

(□) pH = 2.5, (0) pH = 3.0.

Figure 6. Comparison of sorption and coagulation data obtained with Min-U-Sil-5 suspensions (20 g/l) at pH 2.5. The changes in refiltration time (0) and fractional surface coverage (□) as a function of the concentration of iron(III) applied are presented. Sorption curves are calculated from Equation 17, using Γ_m and K obtained from Figure 5, and assuming Min-U-Sil-5 concentration of 20 g/l (solid curve) and 0.2 g/l (dashed curve). The data indicate that sorption may influence coagulation and restabilization.

Figure 7. Equilibrium composition of a solution to which 10^{-3} moles/liter of iron(III) has been added, and the pH adjusted with acid or base. The diagram has been calculated using representative values (65) for the equilibrium constants for solubility and hydrolysis equilibria.

Figure 8. Representative curves for the removal of iron(III) species during filtration through packed columns of glass beads. Changes in Fe(III) in the filtrate are presented as a function of filtration time at various pH values. (0) = fresh iron(III) dispersions, (Δ) = iron(III) dispersions aged 4 hours, $[Fe(III)]_o$ = concentration of iron(III) applied to the filters. Ionic strength $\cong 3 \times 10^{-3}$.

Figure 9. Representative curves describing the effect of sulphate ions on the removal of fresh iron(III) species during filtration through packed columns of glass beads. Changes in Fe(III) in the filtrate are presented as a function of filtration time at pH values of 5 and 7. The data indicate that sulphate ions can improve filtration of iron(III) species at pH 5. Experiments conducted at pH 9.5, like those presented at pH 7.0, showed no significant sulphate effects. (○) $[SO_4^{2-}] = 0$, (□) $[SO_4^{2-}] = 10^{-5}M$, (■) $[SO_4^{2-}] = 10^{-4}M$, (△) $[SO_4^{2-}] = 10^{-3}M$. Ionic strength = 3×10^{-3}.

Figure 10. Anion effects in the filtration of preformed iron(III) precipitates through sand beds. Changes in bed penetration and head loss are presented as a function of the total quantity of iron(III) applied to the filters at pH 5. The abscissa is calculated from the product of flow rate, filtration time, and applied iron(III) concentration. ( ) = demineralized water, (○) = 25 mg/l phosphate, ( ) = 25 mg/l chloride, ( ) = 25 mg/l sulphate.

Figure 11. Anion effects in the filtration of preformed iron(III) precipitates through sand beds. Changes in bed penetration and head loss are presented as a function of the total quantity of iron(III) applied to the filters at pH 7. The abscissa is calculated from the product of flow rate, filtration time, and applied iron(III) concentration. (●) = demineralized water, (○) = 25 mg/l phosphate, (▲) = 25 mg/l chloride, (△) = 25 mg/l sulphate.

Figure 12. Anion effects in the filtration of preformed iron(III) precipitates through sand beds. Changes in bed penetration and head loss are presented as a function of the total quantity of iron(III) applied to the filters at pH 9.5. The abscissa is calculated from the produce of flow rate, filtration time, and applied iron(III) concentration. (●) = demineralized water, (○) = 25 mg/l phosphate, (▲) = 25 mg/l chloride, (△) = 25 mg/l sulphate.

Figure 13. The effects of phosphate ions on the filtration of preformed iron(III) precipitates through sand beds. Changes in bed penetration are presented as a function of the total quantity of iron(III) applied to the filters at pH 5. The abscissa is calculated from the product of flow rate, filtration time, and applied iron(III) concentration. (●) = demineralized water, (▲) = 10^{-4}M phosphate, (△) = 5 x 10^{-4}M phosphate, and (0) = 10^{-3}M phosphate. Increasing phosphate concentrations produced increasing penetration rates and decreased clogging rates.

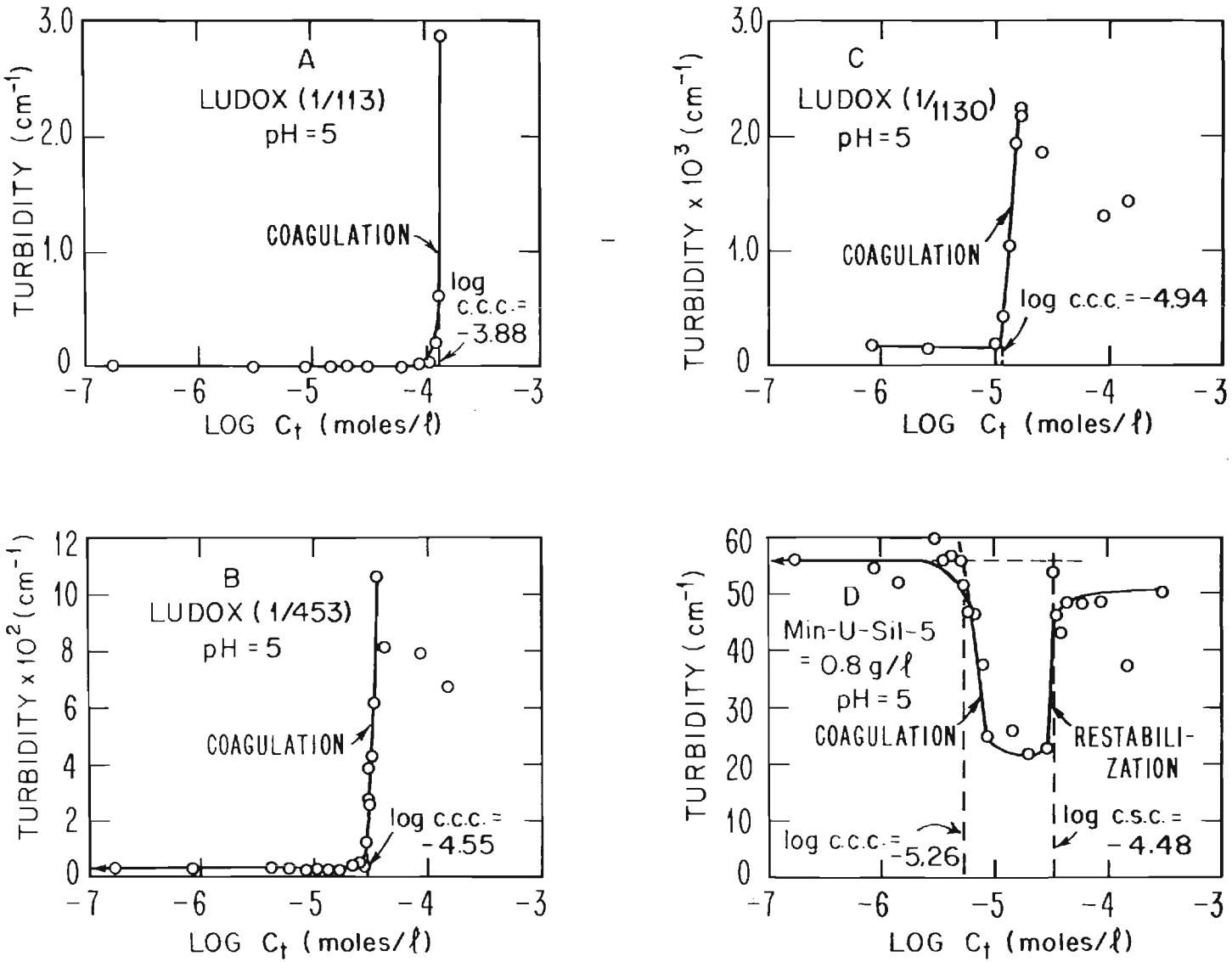

A
LUDOX (1/113)
pH = 5
COAGULATION
log c.c.c. = -3.88
TURBIDITY (cm⁻¹)
LOG C_t (moles/ℓ)
C
LUDOX (1/1130)
pH = 5
COAGULATION
log c.c.c. = -4.94
TURBIDITY x 10³ (cm⁻¹)
LOG C_t (moles/ℓ)
B
LUDOX (1/453)
pH = 5
COAGULATION
log c.c.c. = -4.55
TURBIDITY x 10² (cm⁻¹)
LOG C_t (moles/ℓ)
D
Min-U-Sil-5
= 0.8 g/ℓ
pH = 5
COAGULATION
RESTABILI-ZATION
log c.c.c. = -5.26
log c.s.c. = -4.48
TURBIDITY (cm⁻¹)
LOG C_t (moles/ℓ)

Figure 1

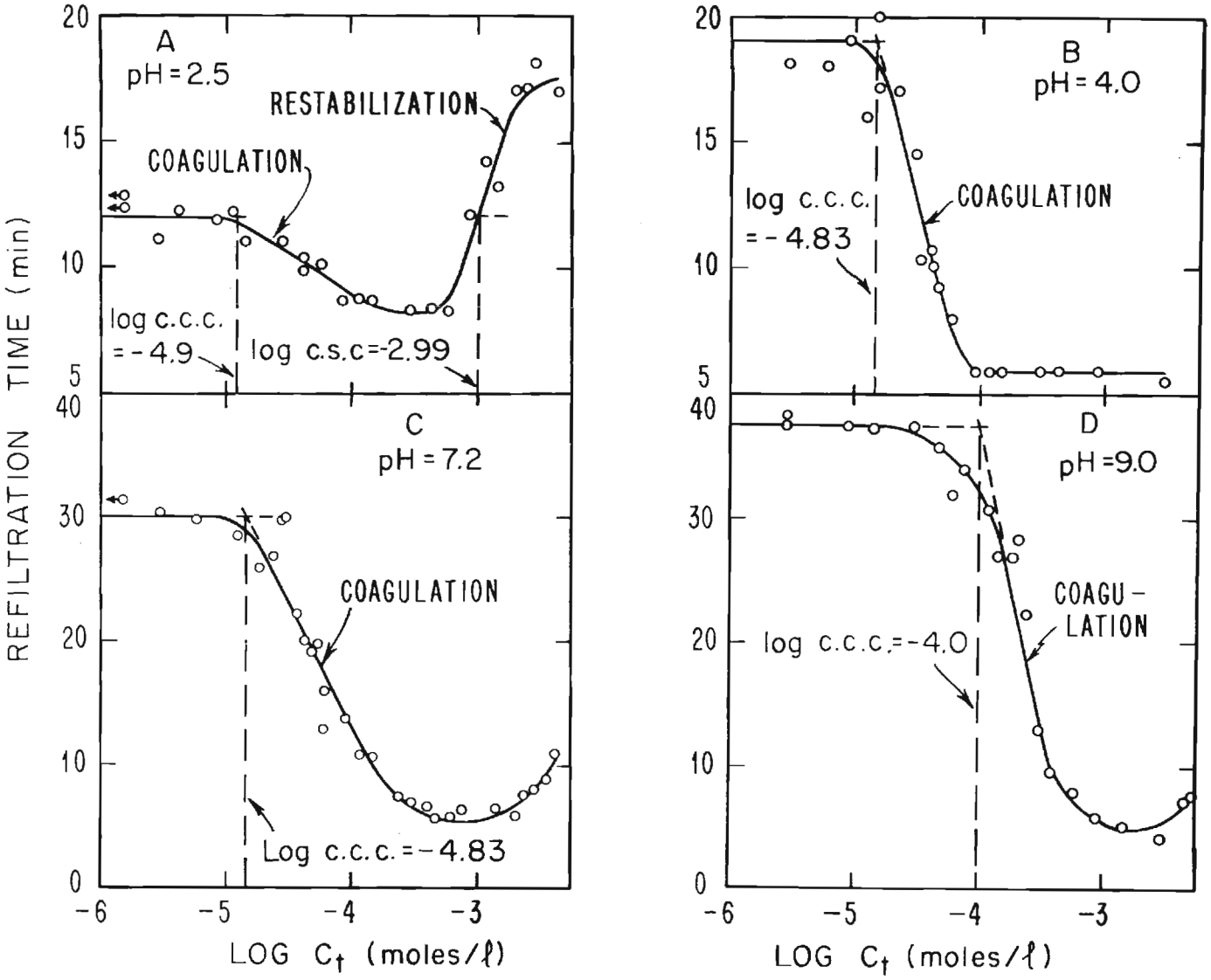

A
pH = 2.5
RESTABILIZATION
COAGULATION
log c.c.c.
= - 4.9
log c.s.c=-2.99
B
pH = 4.0
log c.c.c.
= - 4.83
COAGULATION
C
pH = 7.2
COAGULATION
Log c.c.c. = - 4.83
D
pH = 9.0
COAGU -
LATION
log c.c.c. = - 4.0
REFILTRATION TIME (min)
LOG C_t (moles/ℓ)
LOG C_t (moles/ℓ)

Figure 2

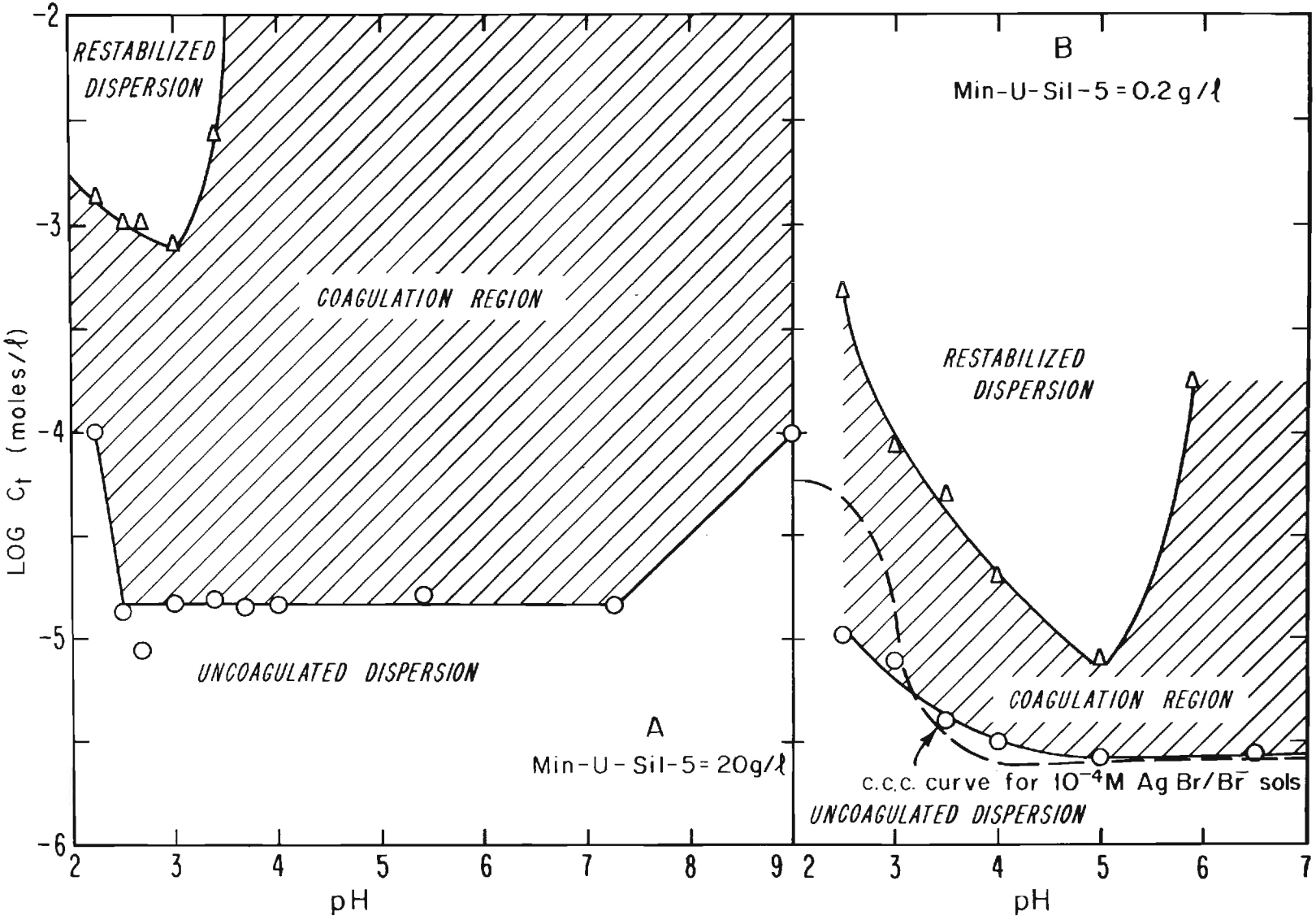

RESTABILIZED DISPERSION
COAGULATION REGION
UNCOAGULATED DISPERSION
A
Min-U-Sil-5 = 20g/ℓ
B
Min-U-Sil-5 = 0.2 g/ℓ
RESTABILIZED DISPERSION
COAGULATION REGION
c.c.c. curve for 10^{-4}M Ag Br/Br^- sols
UNCOAGULATED DISPERSION
LOG C_t (moles/ℓ)
-2
-3
-4
-5
-6
2
3
4
5
6
7
8
9
pH
pH

Figure 3

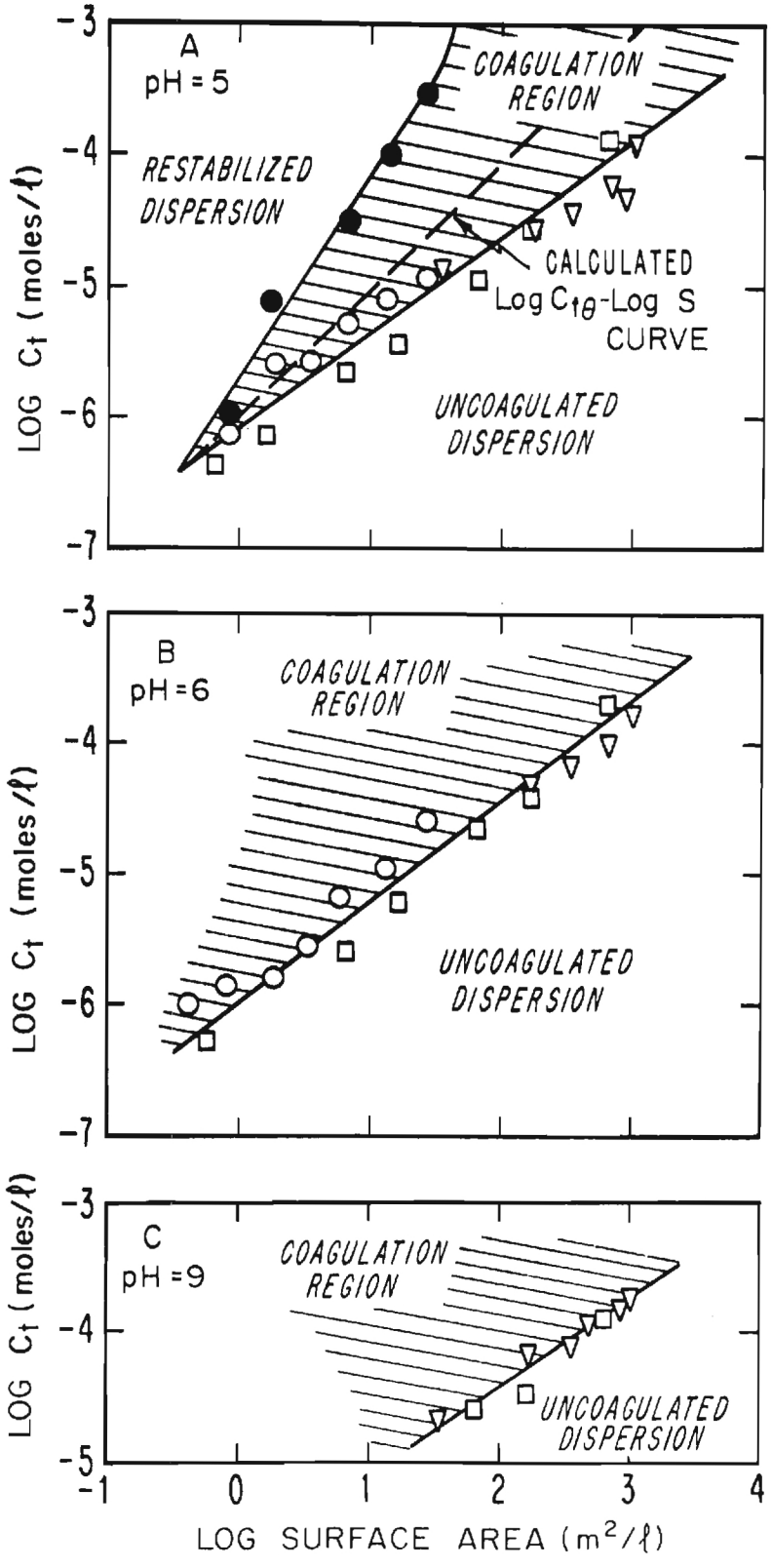

A
pH = 5
COAGULATION REGION
RESTABILIZED DISPERSION
CALCULATED
Log $C_{t\theta}$-Log S
CURVE
UNCOAGULATED DISPERSION
B
pH = 6
COAGULATION REGION
UNCOAGULATED DISPERSION
C
pH = 9
COAGULATION REGION
UNCOAGULATED DISPERSION
LOG C_t (moles/ℓ)
-3
-4
-5
-6
-7
-1
0
1
2
3
4
LOG SURFACE AREA (m^2/ℓ)

Figure 4

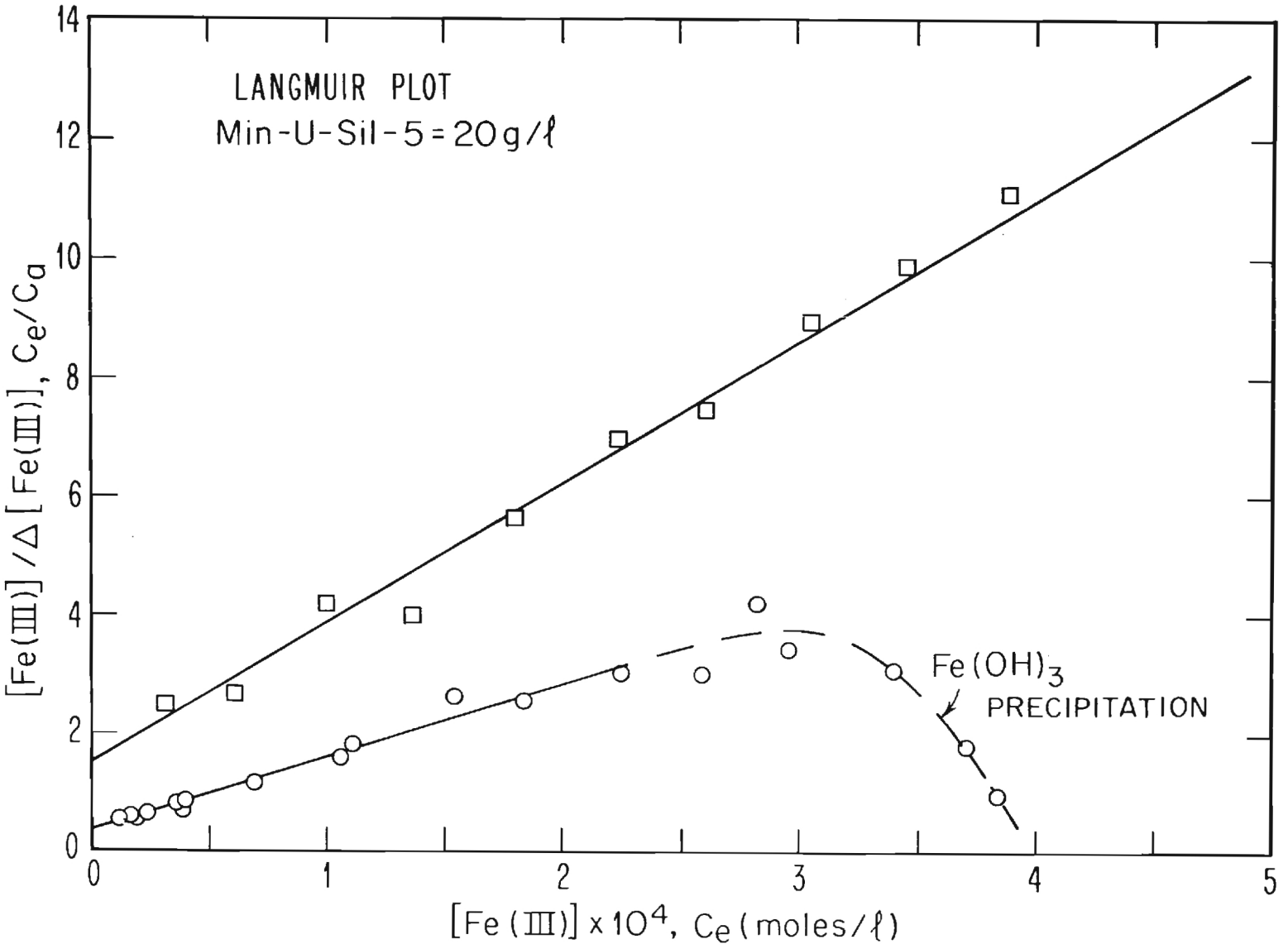

LANGMUIR PLOT
Min-U-Sil-5 = 20 g/ℓ
Fe(OH)3
PRECIPITATION
[Fe(III)] /Δ [Fe(III)], Ce/Ca
[Fe(III)] x 10^4, Ce (moles/ℓ)
0
2
4
6
8
10
12
14
1
3
5

Figure 5

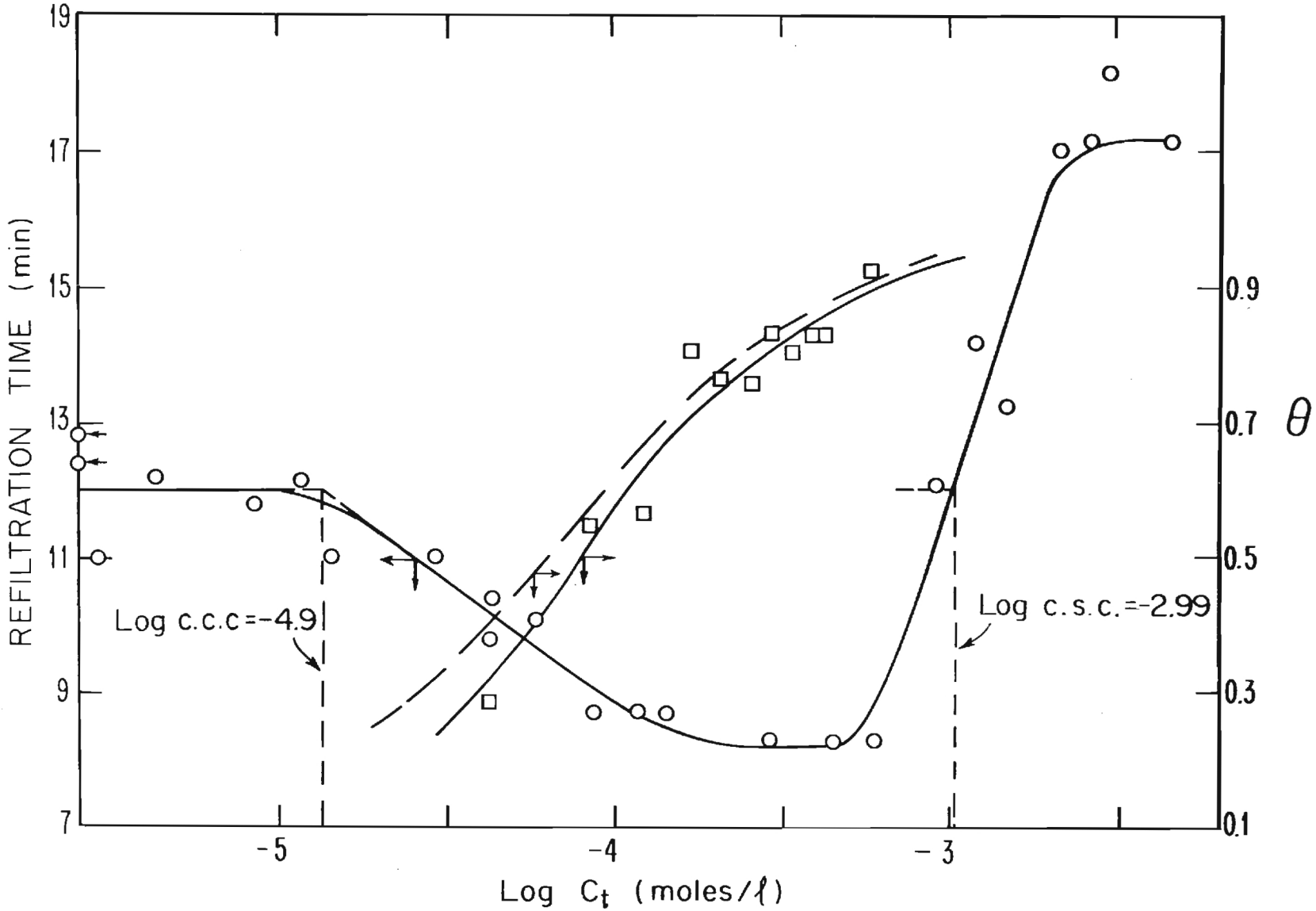
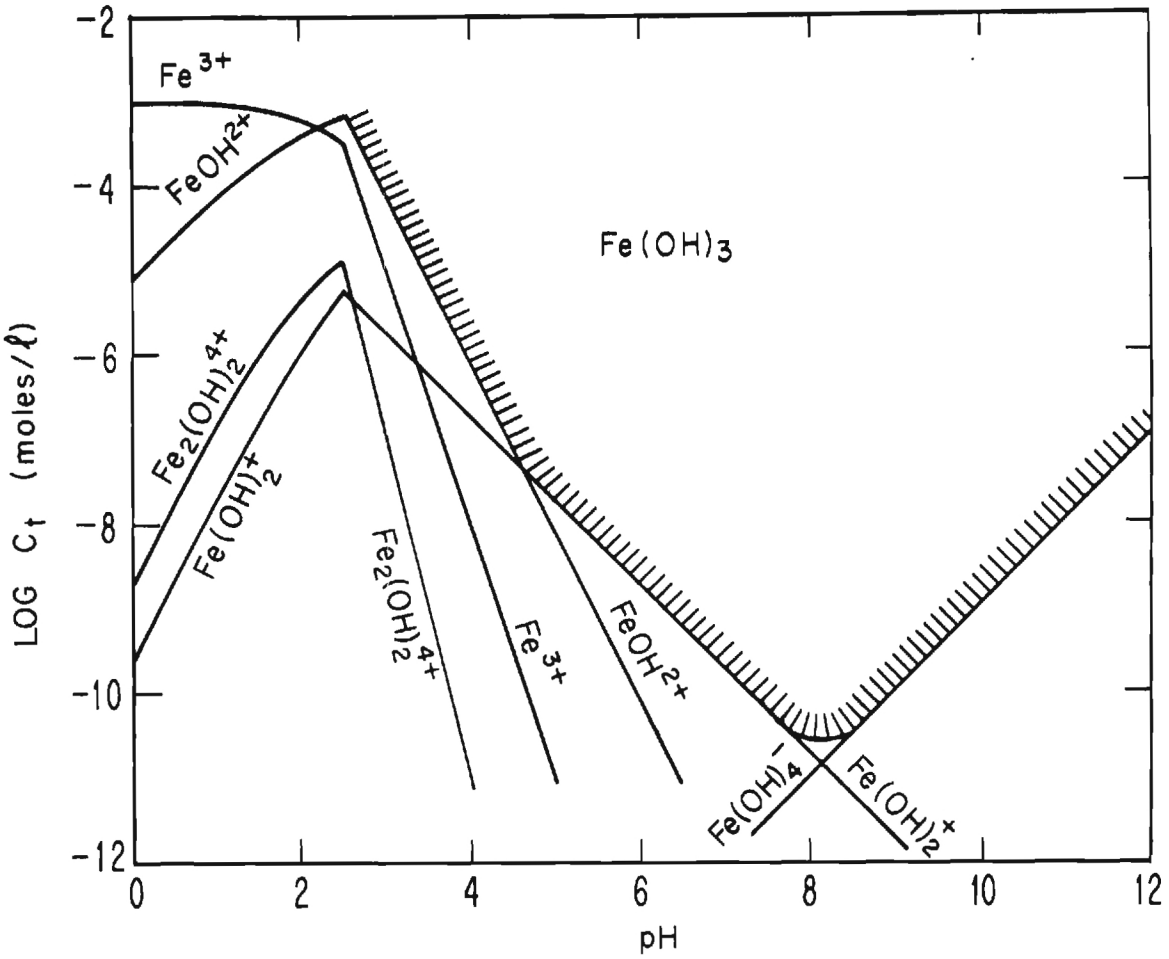

REFILTRATION TIME (min)
19
17
15
13
11
9
7
0.9
0.7
θ
0.5
0.3
0.1
Log c.c.c=-4.9
Log c.s.c.=-2.99
-5
-4
-3
Log C_t (moles/ℓ)

Figure 6



IRON(III) EQUILIBRIA

REACTION	EQUILIBRIUM CONSTANT
$Fe^{3+} + 2H_2O = Fe(OH)^{2+} + H_3O^+$	6.8×10^{-3}
$Fe(OH)^{2+} + 2H_2O = Fe(OH)_2^+ + H_3O^+$	2.6×10^{-5}
$2Fe^{3+} + 4H_2O = Fe_2(OH)_2^{4+} + 2H_3O^+$	1.4×10^{-3}
$Fe(OH)_3(s) = Fe^{3+} + 3OH^-$	10^{-38}
$Fe(OH)_3(s) + OH^- = Fe(OH)_4^-$	10^{-5}

Figure 7

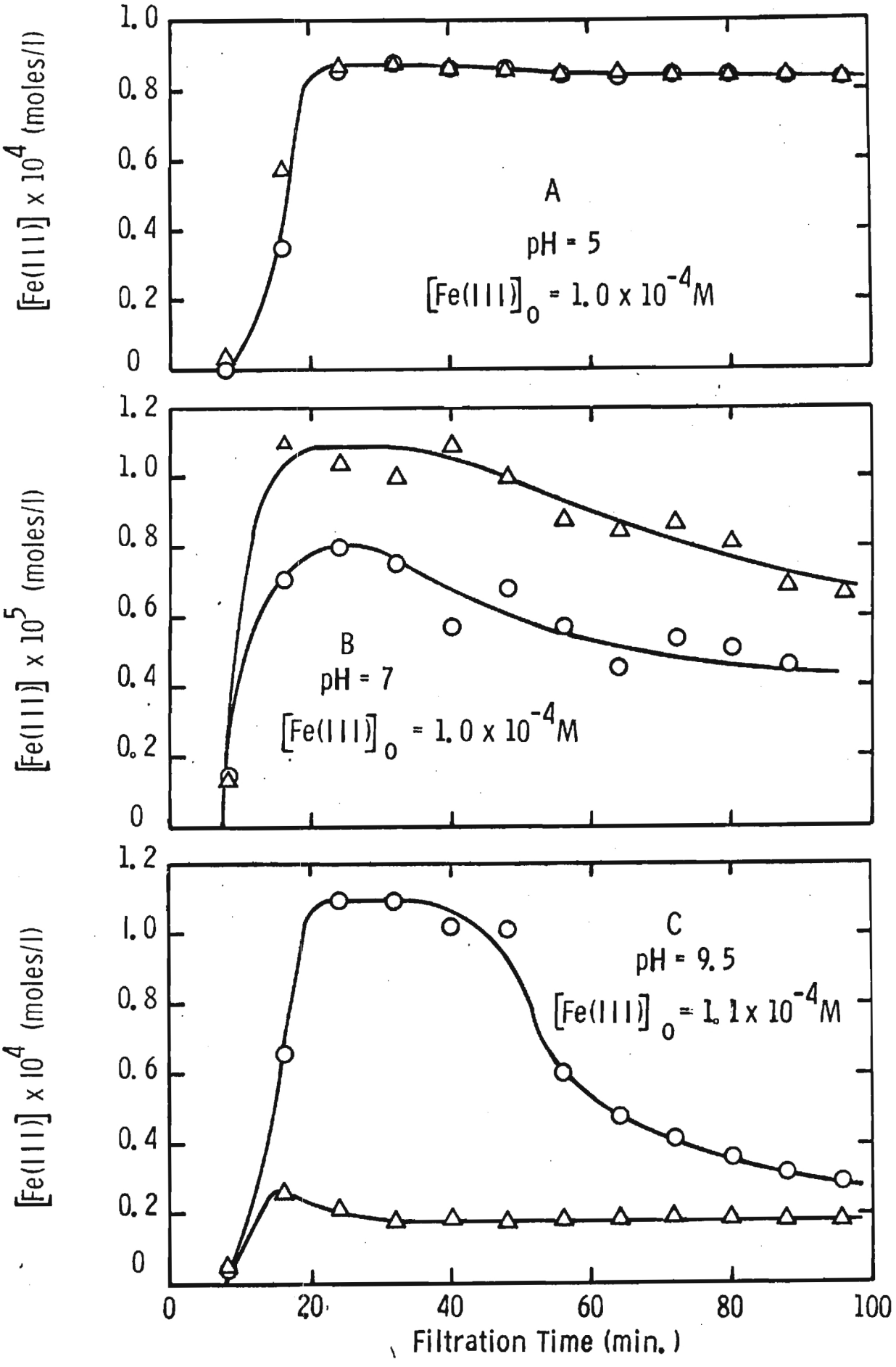

[Fe(III)] x 10^4 (moles/l)
1.0
0.8
0.6
0.4
0.2
0
A
pH = 5
[Fe(III)]0 = 1.0 x 10^-4 M
[Fe(III)] x 10^5 (moles/l)
1.2
1.0
0.8
0.6
0.4
0.2
0
B
pH = 7
[Fe(III)]0 = 1.0 x 10^-4 M
[Fe(III)] x 10^4 (moles/l)
1.2
1.0
0.8
0.6
0.4
0.2
0
C
pH = 9.5
[Fe(III)]0 = 1.1 x 10^-4 M
0
20
40
60
80
100
Filtration Time (min.)

Figure 8

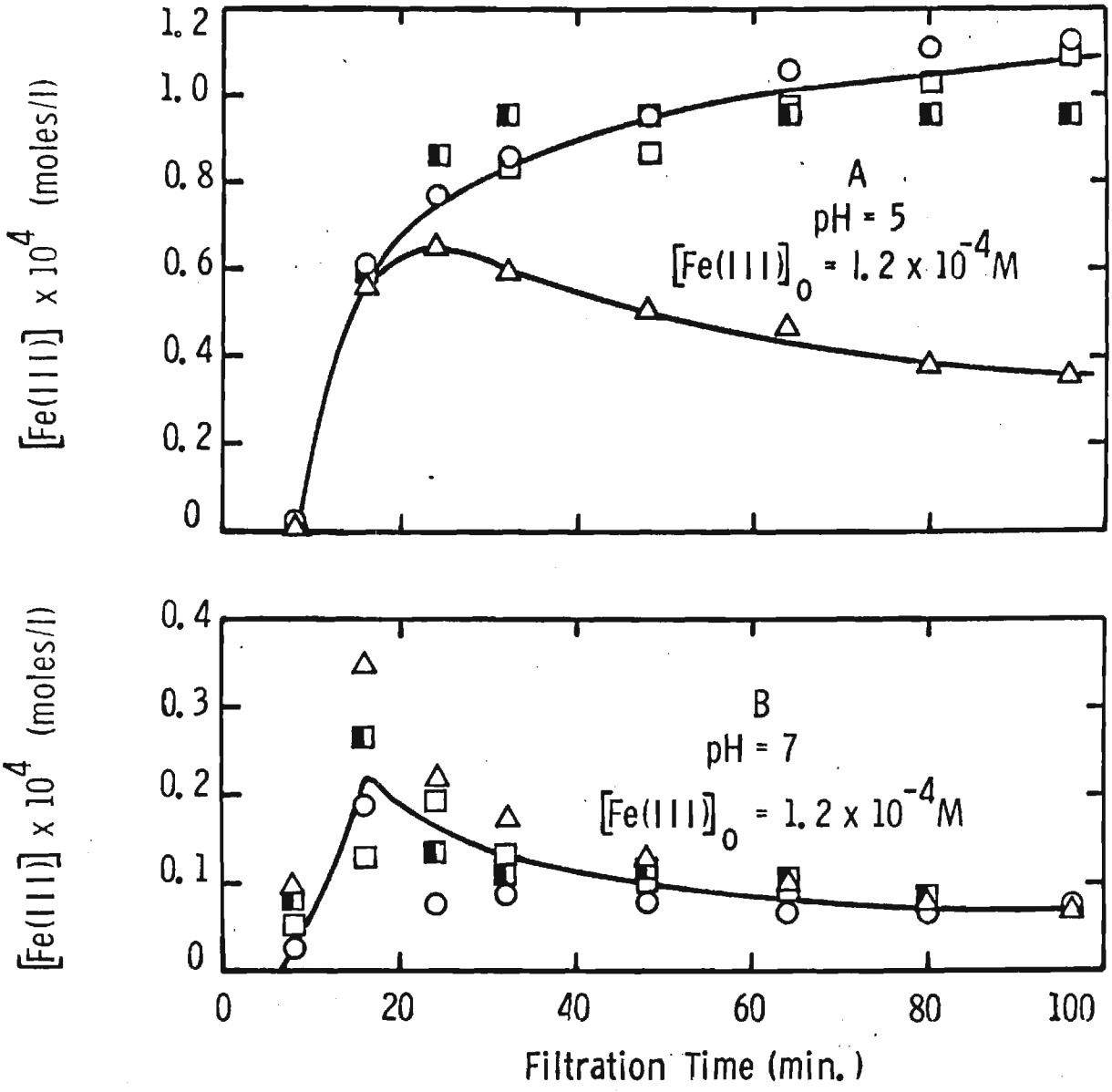

[Fe(III)] x 10^4 (moles/l)
1.2
1.0
0.8
0.6
0.4
0.2
0
A
pH = 5
[Fe(III)]0 = 1.2 x 10^-4 M
[Fe(III)] x 10^4 (moles/l)
0.4
0.3
0.2
0.1
0
B
pH = 7
[Fe(III)]0 = 1.2 x 10^-4 M
0
20
40
60
80
100
Filtration Time (min.)

Figure 9

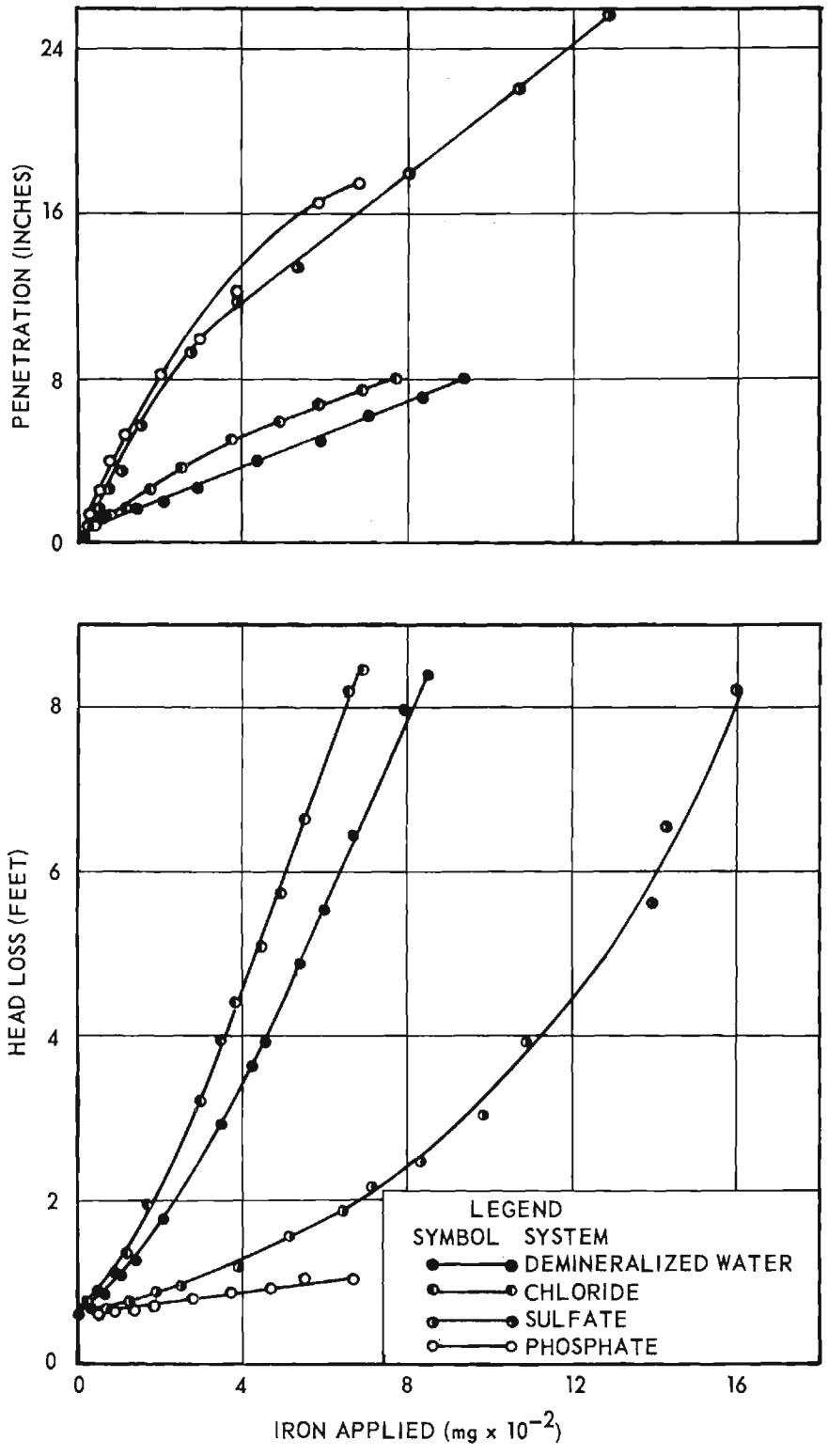

PENETRATION (INCHES)
24
16
8
0
HEAD LOSS (FEET)
8
6
4
2
0
0
4
8
12
16
IRON APPLIED (mg x 10^{-2})
LEGEND
SYMBOL SYSTEM
DEMINERALIZED WATER
CHLORIDE
SULFATE
PHOSPHATE

Figure 10

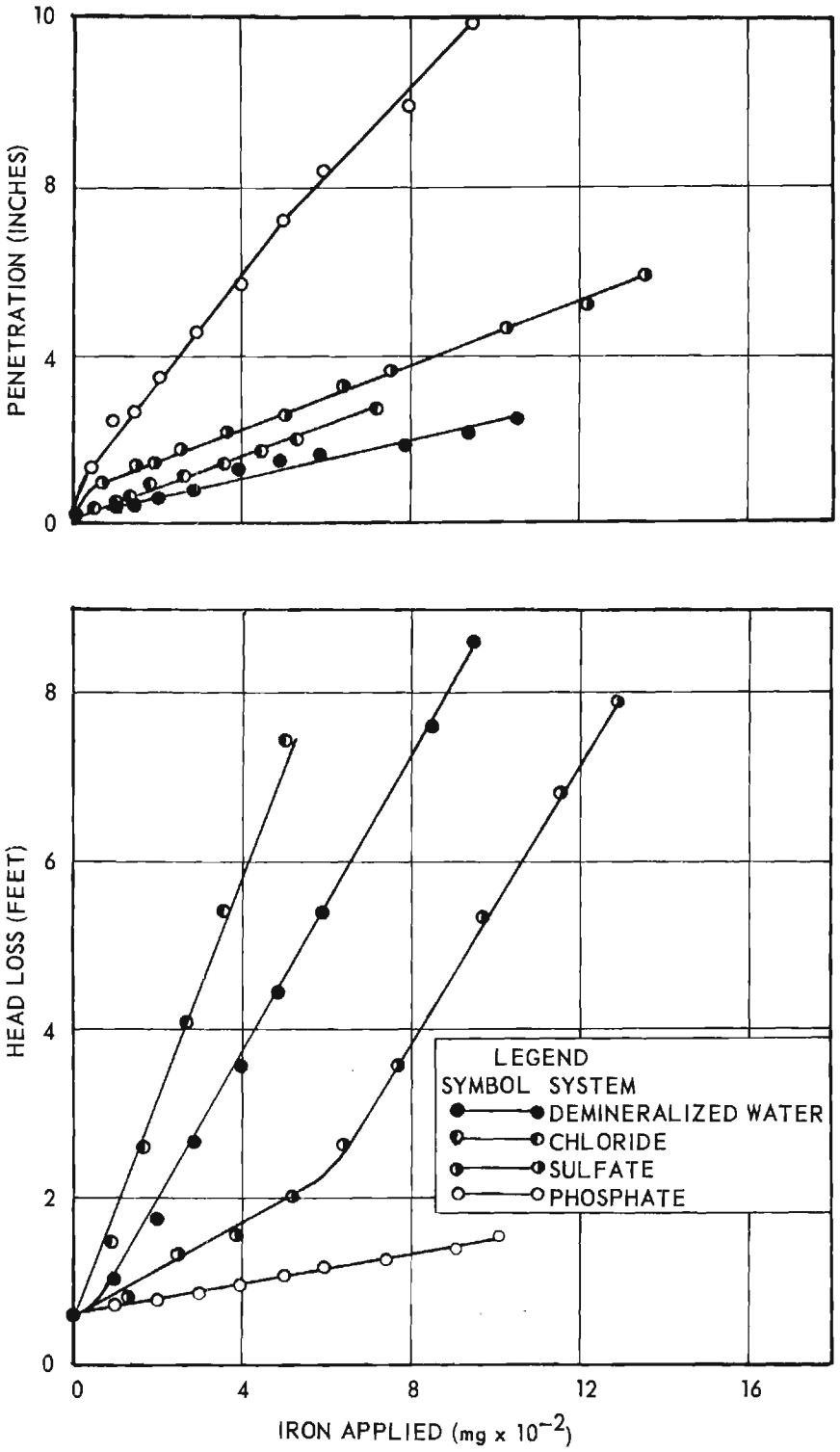

PENETRATION (INCHES)
10
8
4
0
HEAD LOSS (FEET)
8
6
4
2
0
0
4
8
12
16
IRON APPLIED (mg x 10^{-2})
LEGEND
SYMBOL SYSTEM
DEMINERALIZED WATER
CHLORIDE
SULFATE
PHOSPHATE

Figure 11

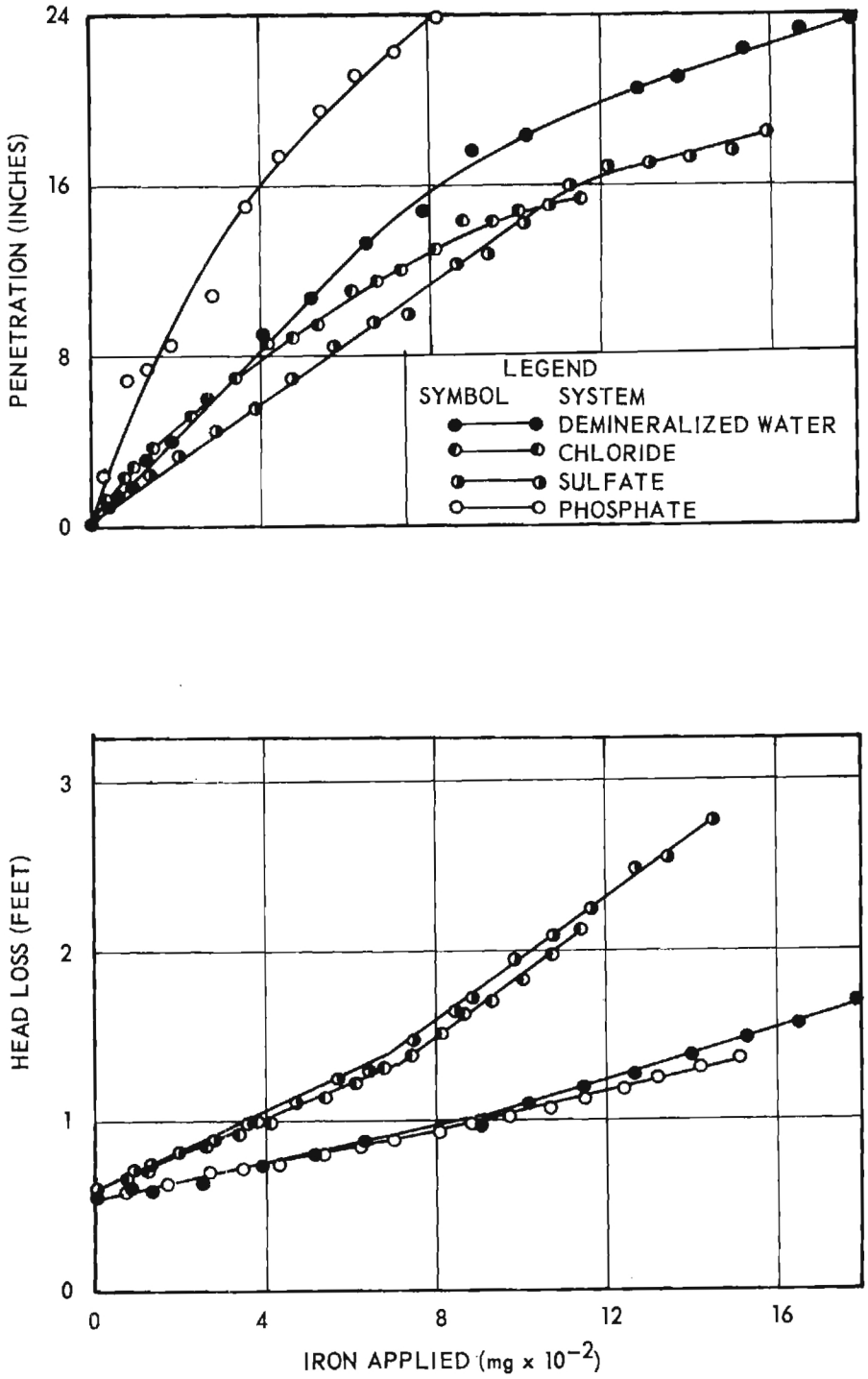

PENETRATION (INCHES)
24
16
8
0
LEGEND
SYMBOL SYSTEM
DEMINERALIZED WATER
CHLORIDE
SULFATE
PHOSPHATE
HEAD LOSS (FEET)
3
2
1
0
0
4
8
12
16
IRON APPLIED (mg x 10^{-2})

Figure 12

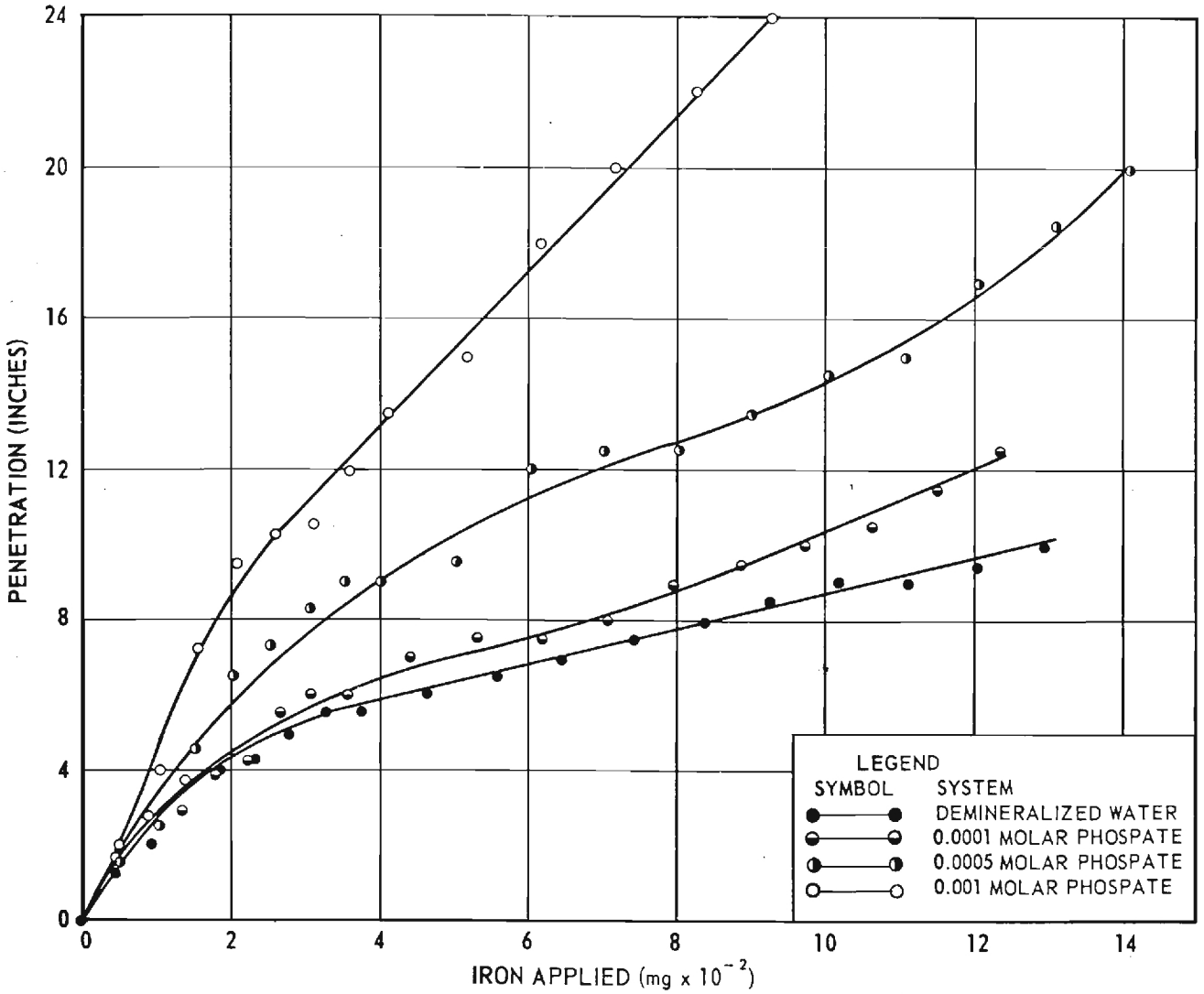

PENETRATION (INCHES)
24
20
16
12
8
4
0
0
2
4
6
8
10
12
14
IRON APPLIED (mg x 10⁻²)
LEGEND
SYMBOL
SYSTEM
DEMINERALIZED WATER
0.0001 MOLAR PHOSPATE
0.0005 MOLAR PHOSPATE
0.001 MOLAR PHOSPATE

Figure 13

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PUBLICATIONS

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1. *O'Melia, C. R., and Crapps, D. K., "Some Chemical Aspects of Rapid Sand Filtration," J. Amer. Water Works Assoc., 56, 1326-1344 (1964).

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